EXPLORING THE IMPACTS OF STREAM-LAKE INTERACTIONS ON THE BIOGEOCHEMISTRY OF ARCTIC HEADWATER RIVER NETWORKS ON THE NORTH SLOPE OF ALASKA

By

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ABSTRACT

EXPLORING THE IMPACTS OF STREAM-LAKE INTERACTIONS ON THE BIOGEOCHEMISTRY OF ARCTIC HEADWATER RIVER NETWORKS ON THE NORTH SLOPE OF ALASKA

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As a result of global climate change, the Arctic is warming at twice the rate of the rest of the planet, releasing terrestrially stored carbon and nutrients previously frozen in permafrost. Due to numerous changes including permafrost degradation and increasing precipitation extremes, the flux of carbon and nutrients from land to water are increasing at most large Arctic river outlets. Within these same river networks, emerging indirect evidence show “stream-lake interactions”, streamflow interrupted by lakes nested within a river network, can modify or confound biogeochemical signals observed at river outlets. To better understand how carbon and nutrients are mobilized and transformed, I conducted two studies that explored how stream-lake interactions alter spatial and temporal biogeochemical signals in two permafrost-dominated river networks on the North Slope of Alaska. First, I analyzed spatially extensive water chemistry, including biologically reactive and geogenic solutes, from 2016-2018 in Oksrukuyik Creek watershed. Next, I investigated lake modulation during storm events using novel high-frequency water quality sensors at the inflow and outflow of an Arctic lake (Lake I8) during the 2019 thaw season. I found evidence that stream-lake interactions modulated biogeochemical signals over a thaw season and during storm events. Together, this indicates stream-lake interactions can modify permafrost-derived carbon and nutrients, highlighting the importance of incorporating steam-lake interactions into future landscape biogeochemical studies in the Arctic, as well as global climate change prediction models.

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KEY TO ABBREVIATIONS

C-Q: Concentration-Discharge

CO_2: Carbon Dioxide

DO: Dissolved Oxygen

DOC: Dissolved Organic Carbon

TDN: Total Dissolved Nitrogen

NO_3^-: Nitrate

NH_4^+: Ammonium

DON: Dissolved Organic Nitrogen

TDP: Total Dissolved Phosphorous

SRP: Soluble Reactive Phosphorous

SO_4^{2-}: Sulfate

PCTE: Polycarbonate Track Etch

DEM: Digital Elevation Model

GIS: Geographic Information System

ANOVA: Analysis of Variance

DRS: Dissolved Reactive Silicon

LTER: Long Term Ecological Research

RT: Residence Time

PVC: Polyvinyl Chloride

PLSR: Partial Least Square Regression

β: Slope

CV: Coefficient of Variation

HI: Hysteresis Index

FI: Flushing Index

IQR: Interquartile Range

CHAPTER 1: INTRODUCTION

The Arctic is a vast and globally unique region defined by strong seasonality

The Arctic is an expansive biome with a unique climate and geography. First, many parts of the Arctic are underlain by varying presence of permafrost, which is a defining feature of many Arctic ecosystems. Permafrost is soil that has been frozen for at least two consecutive years (Zhang et al., 1999; Hobbie and Kling, 2014), and the permafrost coverage can be sporadic (10-50% of landscape area), discontinuous (50-90%), or continuous (>90%) (Obu et al., 2019). Altogether, permafrost is present underneath 25% of the Northern Hemisphere's terrestrial land surface, nearly all of which is in the Arctic (Gruber, 2012). Permafrost soils represent a major global nutrient and carbon reservoir, holding nearly 1,600 Pg of Carbon, which is equivalent to twice what is currently in the atmosphere as CO_2 and other gases (Tarnocai et al., 2009; Schuur et al., 2015; Turetsky et al., 2019). In addition to the unique physical constraint of permafrost, Arctic ecosystems are also characterized by a distinct seasonal pattern. At high latitudes, winters are long, dark, and cold; on the North Slope of Alaska specifically, rivers freeze entirely from mid-October through late May. Then, rivers flow during a brief and constrained thaw season the rest of the year, with very long days including up to 24 hours of sunlight at the peak of the growing season. Therefore, the Arctic thaw season is the period when most hydrologic and biogeochemical activity occurs, as temperature and light limitations are alleviated, and liquid water flows through terrestrial and aquatic ecosystems (Kling, 2009).

The Arctic is undergoing rapid, systematic changes

The Arctic environment is warming at twice the rate of lower latitudes, with annual temperatures predicted to increase to 9.8 ± 2ºC by 2100 (Overland et al., 2019). Broadly, a warming Arctic will experience intensified extent and duration of disturbance regimes such as wildfires (Kling, 2009; Rawlins et al., 2010; Rodríguez-Cardona et al., 2020), altered structure of terrestrial vegetation communities (Jia et al., 2003; Ernakovich et al., 2014; Koven et al., 2015), and extended flow seasons with earlier snowmelt and later refreeze (Chae et al., 2014; Arndt et al., 2019). Arctic landscapes will also undergo dramatic changes to both the physical landscape and an intensification of the hydrologic cycle, which I describe in greater detail below.

There is a growing recognition that climate change will lead to drastic changes in the extent and condition of Arctic permafrost (Jorgenson et al., 2010; Hobbie and Kling, 2014). Arctic warming increases the rate of distributed permafrost thaw, resulting in deepening of the "active layer", the layer of soil that thaws seasonally through which water and nutrients can be easily transported (Hobbie and Kling, 2014). A thickening active layer opens more potential avenues where water can flow, increasing hydrologic connectivity between terrestrial and stream ecosystems. Thicker active layers allow water to reach deeper soil layers storing previously inaccessible permafrost carbon and nutrients. Maximum active layer depth is expected to increase across much of thawing permafrost regions (Harms and Jones, 2012; Koven et al. 2015). Rising temperatures and degrading permafrost can further result in an increasing incidence of abrupt permafrost thaw or "thermokarst" (Bowden et al., 2008). A thermokarst is a topographic depression caused by catastrophic permafrost thaw. Thermokarst areas are known for rapidly releasing terrestrial organic matter and nutrients into aquatic networks, and are significant sources of atmospheric greenhouse gas emissions, including carbon dioxide and methane (Kling et al., 1991; Grosse et al., 2013). Specifically, thermokarst on the North Slope of Alaska, which extends from the Brooks Range northward to the Arctic Ocean, releases 70-150 kg of Carbon per square meter per year (Kling, 2009; Hugelius et al., 2014, Abbott and Jones, 2015). Large and sustained thermokarst formation can eventually produce thermokarst lakes (Grosse et al., 2013; Rowley et al., 2015). The North Slope is spotted with tens of thousands of thermokarst lakes, yet it is unclear how size and density of thermokarst lakes will change as ground ice continues to thaw (Kling, 2009; Huryn and Hobbie, 2012; Grosse et al., 2013). This uncertainty stems from the interactions between increased hydrologic connectivity, temperature, and precipitation, as well as changing Arctic geomorphology and vegetation communities (Riordan et al., 2006; Kling, 2009; Grosse et al., 2013).

Additionally, as the Arctic undergoes progressive warming, the frequency and duration of heavy precipitation events is increasing in a process known as hydrologic “intensification” (Solomon et al., 2007; Rawlins et al., 2010; Bring et al., 2016). Climate models predict increasing frequency and intensity of precipitation events (Rawlins et al., 2010; Bintanja et al., 2020), and these effects are expected to amplify in the near future (IPCC, 2013; Ranasinghe et al., 2021). Effectively, while thawing permafrost may release stored nutrients from a deep freeze as described above, precipitation events increase hydrologic lateral connectivity between land and water, mobilizing hydrologically available nutrients towards the stream channel and increasing transport of carbon and nutrients to downstream aquatic networks (Beel et al., 2020; Knapp et al., 2020). Amplified precipitation regimes and thaw season dynamics have local, regional, and global implications for the fate and transport of water and biogeochemical significant solutes mobilized from the terrestrial environment. For example, longer thaw seasons lead to higher hydrologic potential to transport permafrost soil carbon and nutrients into aquatic ecosystems, thus enhancing the carbon cycle climate feedback loop (Koven et al., 2015; Schuur et al., 2015).

When taken together, the biophysical feedbacks between landscape change and increased precipitation will impact the biogeochemistry of high-latitude rivers (ACIA, 2005; Rawlins et al., 2010; Wrona et al., 2016). The transport and transformation of permafrost-derived carbon and nutrients is a major source of uncertainty in earth system models that aim to predict the response of global biogeochemical cycles to climate change (Kicklighter et al., 2013; Metcalf et al., 2018). Therefore, a major open research question for the Arctic science community is how we can better constrain ecosystem carbon and nutrient fluxes as Arctic ecosystems experience increased permafrost thaw and hydrologic cycle intensification (Rawlins et al., 2010).

Arctic rivers can be used as indicators of landscape change, but stream-lake interactions are a virtual unknown

While the Arctic is a vast region, changes in stream chemistry can generally be used as sentinels of aquatic and terrestrial effects (Williamson et al., 2008; Hartmann et al., 2014). More specifically, water-mediated lateral (terrestrial to aquatic) and longitudinal (upstream to downstream) connections between ecosystem components are expressed in river network chemistry measured at a watershed outlet. Importantly, Arctic aquatic ecosystems (e.g., streams, rivers and lakes) are often carbon-rich and nutrient-poor, and are strongly influenced by nutrient and organic matter inputs from the surrounding terrestrial environment (Kling, 2009; Hobbie and Kling, 2014). However, with increased permafrost sourcing and hydrologic mobilization, the availability of carbon and nutrients to downstream export will likely change (Wrona et al., 2016). While long-term records of Arctic river chemistry are exceedingly rare, the observed biogeochemical concentrations and annual fluxes are already increasing across most Arctic rivers where these records exist (Frey et al., 2007; McNamara et al., 2008; Toohey et al., 2016), suggesting changes to these terrestrial-aquatic linkages. Therefore, river network signals may provide a real-time window into changing Arctic regimes.

There is an open knowledge gap of how Arctic lakes that are nested within a river network may interrupt longitudinal flow paths and alter biogeochemical processing, thereby changing the river chemistry that is measured at the watershed outlet. Evidence of stream-lake interactions from temperate systems have indicated that lakes can act as both sources or sinks of aquatic nutrients, and that these processes can vary with time between a lake and its streams (Goodman et al., 2011; Baker et al., 2016). Here I define the distinction between source and sink as a lake's modulation effect on biogeochemical signals. When lakes act as a carbon or nutrient "sink", they may retain and remove nutrients from a riverine network through processes including nutrient uptake, denitrification, or burial in sediments (Epstein et al., 2013; Cooke et al., 2016). When a lake behaves as a carbon or nutrient "source", concentrations may increase at lake outlets and consequently in the downstream riverine network, the result of decreased biological activity and nutrient production, lake mixing, sediment resuspension, or export from large rain events (Wurtsbaugh et al., 2005; Baker et al., 2016). For example, during large precipitation events, water and nutrients are mobilized rapidly and can shift a lake toward heterotrophic metabolism (Dahm et al., 2003; Williamson et al., 2014). This switch to heterotrophy increases greenhouse gas emissions (i.e., carbon dioxide (CO_2) and methane (CH_4)) from lakes to the atmosphere (Ojala et al., 2010; Zwart et al., 2017). Additionally, larger lakes with longer water residence time (i.e., lake volume divided by the rate of water loss) may have a higher capacity to modulate biogeochemical concentrations (Paulson and Baker, 1980; Kling et al., 2000, Baker et al., 2016; Zwart et al., 2017). Furthermore, large precipitation events increase lake discharge and shorten residence time, thus increasing nutrient export and reducing time for biogeochemical modulation (Zwart et al., 2017).

Growing, but very limited, evidence suggests that stream-lake interactions modulate carbon and nutrient export from Arctic watersheds (Shogren et al., 2019), yet it is uncertain the role that Arctic lakes play in modulating these intensifying, climate-driven, biogeochemical fluxes (Battin et al., 2009). Exploring solute concentration and fluxes in stream-lake interactions is necessary for improving our understanding and projection of Arctic environmental changes (Kling, 2009; Bring et al., 2016). Hence, this thesis will address the exciting research area of "stream-lake-interactions", asking: *How do lakes change or "modulate" biogeochemical signals in Arctic watersheds of northern Alaska?*

To address this overarching stream-lake interaction question and answer four specific research questions (Table 1), I conducted two studies of stream-lake interactions that had different types of water quality data (i.e., a spatial and temporal data set). Spatially extensive data have been widely used to capture processes and patterns throughout a river network (Abbott et al., 2018) and these types of data are used to address stream-lake interactions across an entire watershed (Question 1; Hypothesis 1, Table 1). On the other hand, high-frequency temporal data provide insightful information into ecosystem and riverine processes that are otherwise difficult to sample (i.e., storm events) (Kirchner et al., 2004; Crawford et al., 2015; Burns et al., 2019) and reveal how a single lake interacts with and modifies stream network chemistry (Question 2; Hypothesis 2, Table 1). Together, spatial and temporal datasets are complementary and beneficial for in-depth examination of the patterns, processes, and variability within an Arctic river network (Shogren et al., 2019).

Table 1: Proposed Research Questions and Hypotheses		
Research Question	**Hypothesis**	**Data Available**
Question 1: *A)* How do biogeochemical signals compare between subcatchments with increasing lake influence? *B)* How does lake residence time modulate biogeochemical signals in a headwater stream system?	**Hypothesis 1:** *A)* Because lakes modulate biogeochemical concentrations, a lake-dominated subcatchment will show higher spatial instability than subcatchments with less lake influence. *B)* Smaller lakes with shorter residence times will show less solute modulation and larger lakes with longer residence times will show a higher modulation effect.	**Spatial (Oksrukuyik Creek):** *A)* Synoptic sampling of water chemistry from 3 subcatchments (high, medium, no lake influence). *B)* Inflow/outflow sampling sites on 3 lakes.
Question 2: *A)* How does an Arctic lake modulate the riverine biogeochemical fluxes during storm event flows? *B)* Do these storm event modulation effects differ between early and late thaw season when active layer and terrestrial ecosystem conditions are vastly different?	**Hypothesis 2:** *A)* Storm events decrease lake residence time, but can increase carbon and nutrient influx, which can temporarily increase internal processing potential. Therefore, based on concentration-discharge (C-Q) relationships and metrics, storm events will flush solutes into a lake, but the lake will process and buffer those solutes. *B)* Numerous lake and riverine processes, as well as hydrologic flow paths, change throughout the Arctic thaw season. Because of deeper flow paths and lake mixing, lake internal processing potential will be greater in late compared to early thaw season storm events.	**Temporal (I-series):** High-frequency water quality and discharge data at inflow and outflow of 1 lake.

General site description

Both study watersheds, Oksrukuyik Creek and the I-series, are located on the North Slope of Alaska, in the northern foothills of the Brooks Range (Figure 1.1). These watersheds are part of the Arctic Long Term Ecological Research (ARC LTER) site at Toolik Field Station. This area is characterized by treeless upland tundra and is underlain with continuous permafrost with well-defined river networks and lakes (Figure 1.2). Mean annual temperature is -7 ºC but ranges

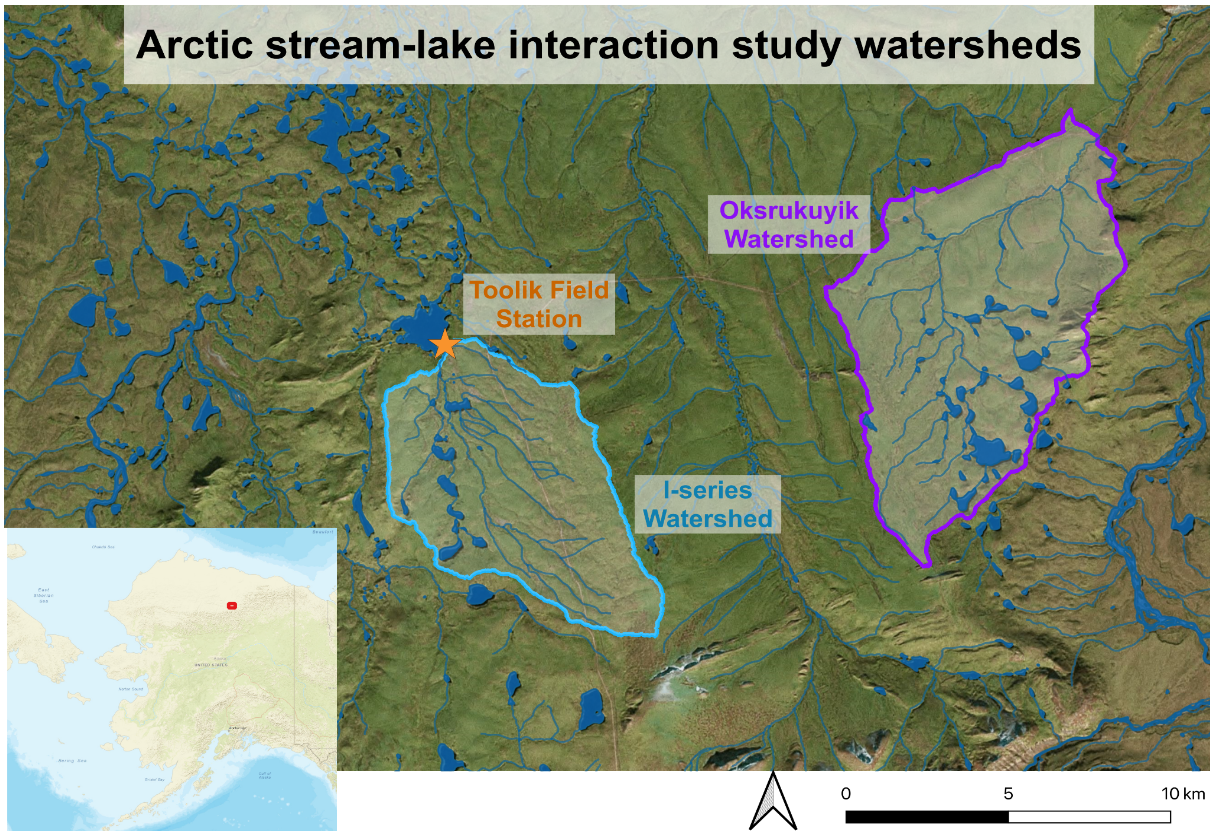

Figure 1.1: Site map of stream-lake interaction study watersheds with respect to Toolik Field Station on the North Slope of Alaska.

from -41 ºC in January to 25 ºC in July. Complete snow cover persists for 7 to 9 months (roughly October to May) when all lakes and streams completely freeze (Hobbie and Kling, 2014). Thaw season lasts roughly four months (May-August) and includes the relatively understudied early and late "shoulder" seasons; early shoulder season is prior to snowmelt and late shoulder season is after plant senescence (Shogren et al., 2020a). The highest precipitation typically occurs between July and August (late thaw season) and annual precipitation is around 290 mm (Environmental Data Center Team 2016). The summertime active layer in this region is roughly 30-50cm thick (Hobbie and Kling, 2014). The data from this study area that were included in my study were collected during the thaw seasons of 2016-2019. Further site-specific details are included below (Section 2.2.1 and 3.2.1). In this study, I use watershed and catchment synonymously, but subcatchment specifically refers to a smaller study area that exists within a study watershed as shown in the site figures.

Figure 1.2: Photos from within Oksrukuyik Creek watershed and I-series watershed that contains Lake I8. Descriptions of each photo follows: A) aerial view of Oksrukuyik Creek watershed, B) Oksrukuyik Creek in May, C) Oksrukuyik Creek in June, D) Oksrukuyik Creek in July, E) I8 inlet looking downstream into Lake I8, and F) Lake I8 in June. Images span most of the thaw season, with low productivity and snow/ice in the channel during the early thaw season, and high productivity with no ice during the late thaw season.

CHAPTER 2: SPATIAL ASSESSMENT OF THE EFFECTS OF STREAM-LAKE INTERACTIONS ON WATERSHED BIOGEOCHEMICAL SIGNALS

2.1. Introduction

Spatially extensive water chemistry data can reveal landscape patterns and provide insight into solute sourcing, mobilization, and variability throughout a river network (Abbott et al., 2018; Shogren et al., 2019). Synoptic stream chemistry sampling is limited in remote areas like the Arctic, where access is difficult (Shogren et al., 2019). Using single river sampling location approaches, such as setting up a monitoring station, are also useful and are more common in the Arctic because they can be easier to access and maintain. However, upstream landscape variability, like lakes in a river network, can make interpretation of downstream monitoring data complicated. For example, upstream lakes can either intensify or buffer solute

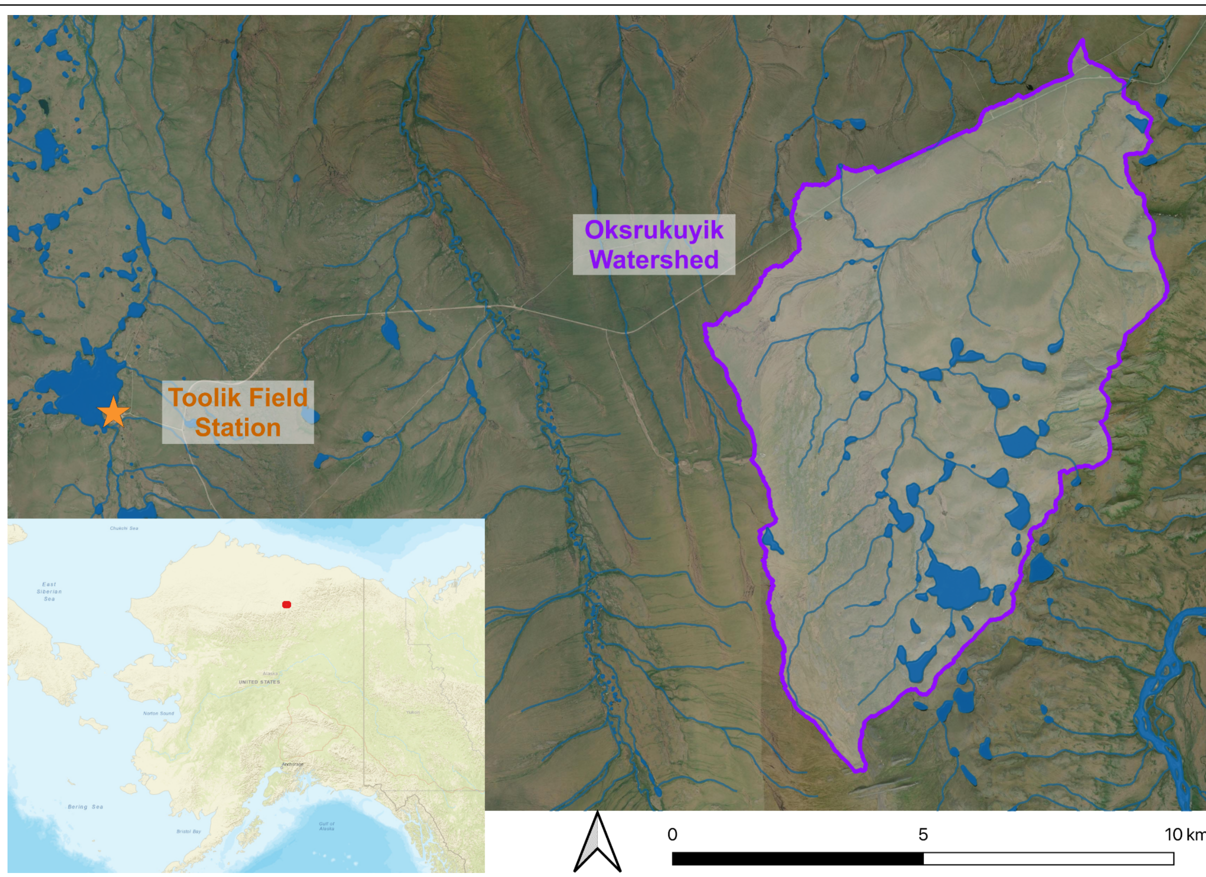

Figure 2.1.1: Site map for Oksrukuyik Creek watershed with respect to Toolik Field Station.

signals, modifying downstream chemical signals (Goodman et al., 2011; Epstein et al., 2013; Baker et al., 2016; Shogren et al., 2019). A prior study in the Arctic found a lake-dominated watershed had larger solute instability and seasonal variation when compared to nearby watersheds with limited or no-lake influence, suggesting lakes can act as both solute producers or removers (Shogren et al., 2019). To further assess how lakes modulate solutes, I leveraged multiple years of spatially extensive synoptic sampling data of 29 locations within a headwater, lake-dominated Arctic watershed (Oksrukuyik Creek watershed; Figure 2.1.1 & Figure 2.2.1).

I examined the spatial patterns of biogeochemical concentrations, with a focus on lake inlet and outlet solute conditions, to assess how lakes transform nutrients throughout the watershed. Specifically, I explored the role of lakes and their residence times in altering nutrient concentrations. I asked: 1a) How do biogeochemical signals compare between subcatchments across a gradient of lake influence, and 1b) How does lake residence time modulate biogeochemical signals in a headwater stream system? (Table 1). To answer these questions, I use all three subcatchments of the Oksrukuyik Creek watershed on the North Slope of Alaska

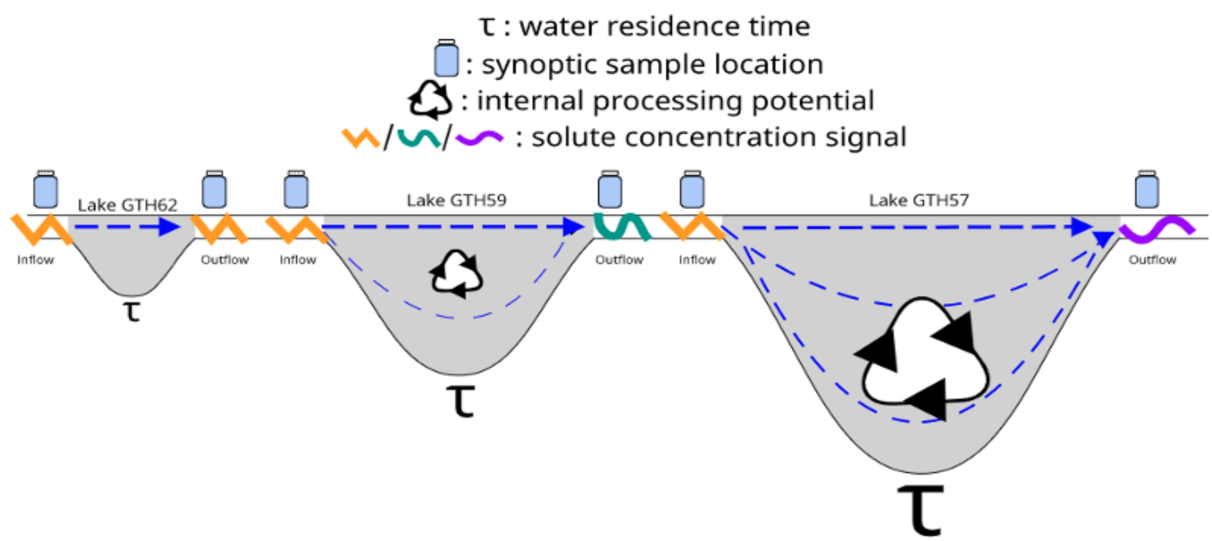

Figure 2.1.2: Conceptual model for the effect of lake size, which is correlated with water residence time[τ] on lake internal processing potential and solute modulation. Internal processing potential increases as a function of τ. Therefore, solute concentration signals are affected by residence times of the lakes.

that have varying stream-lake interactions to compare variability in nutrient processing and spatial stability. Then, within only the high-lake influenced subcatchment, I estimate the residence time of three lakes and compare the net change between lake inflow and outflow (Figure 2.2.2) as a function of their individual residence times. This spatial analysis indicates that multiple types of lakes with different conditions and sizes possess the ability to change nutrient signals moving through stream networks (Figure 2.1.2 - conceptual model).

2.2. Materials and Methods

2.2.1. Site Description

The Oksrukuyik Creek watershed is a low-gradient third-order tundra stream spotted with lakes ranging in size and residence times (Harvey et al., 1998; Hobbie and Kling, 2014; Shogren et al., 2019). It drains roughly 73.5 km^2 and is 12 km in length (Figure 2.1.1). Oksrukuyik Creek drains mainly a rocky substrate and is a clear-water oligotrophic stream that lacks inflow from glacial runoff or mineral springs (Harvey et al., 1998).

Oksrukuyik Creek has three main headwater subcatchments that were delineated to examine the effect of stream-lake interactions on biogeochemical processing (Figure 2.2.1; delineation method description in Section 2.2.3). Subcatchments range from no lake to medium-lake influence to high-lake influence (Balser, 2001). The no lake subcatchment has an area of 5.82 km^2. The intermediate or mid-lake influenced subcatchment drains 26.5 km^2 and lakes cover 6.6% of the subcatchment. Note it has the highest number of lakes (n=15), but they are less densely distributed than the high-lake subcatchment. The high-lake influenced subcatchment, which I used for my second question, had an area of 8 km^2 with nine lakes covering 10% of the area (Figure 2.2.2).

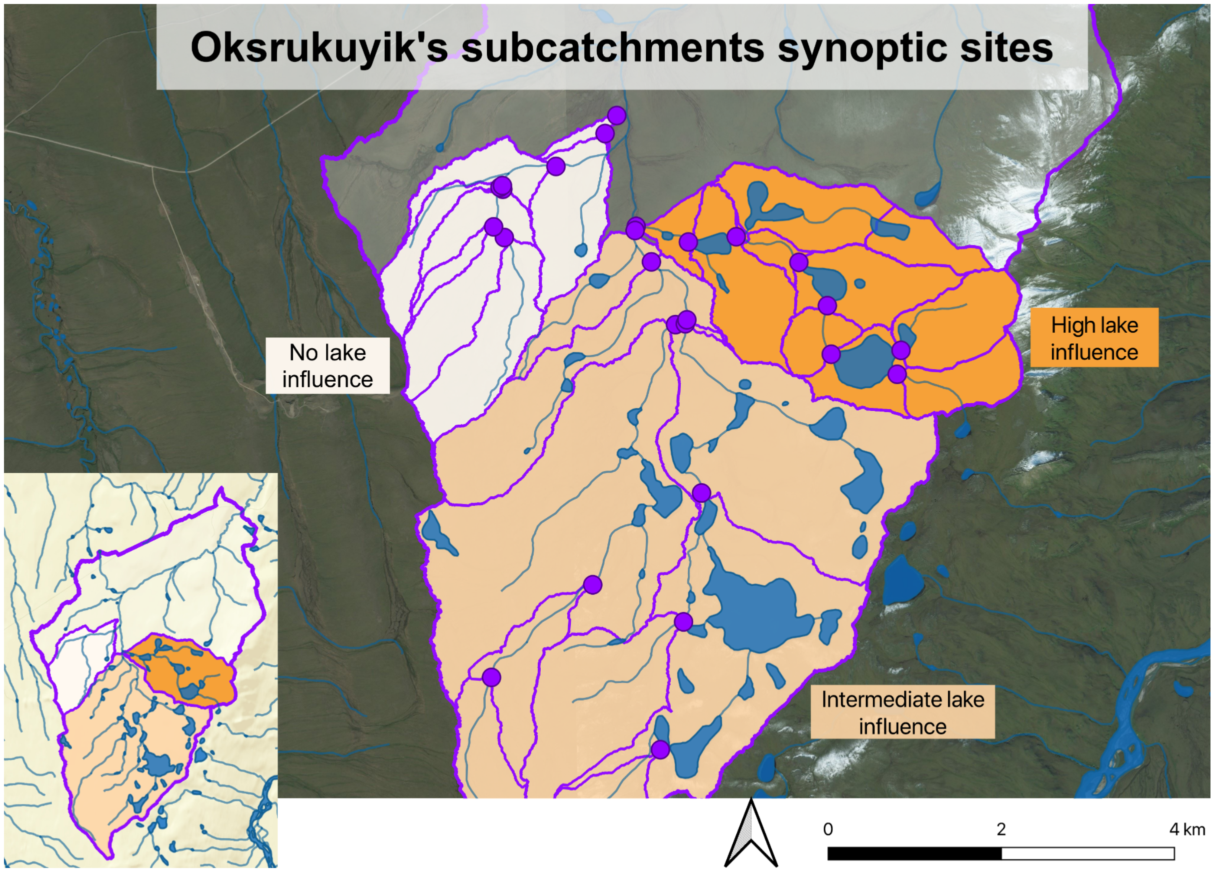

Figure 2.2.1: Oksrukuyik Creek watershed synoptic sampling locations (purple points) and delineated subcatchments with varying stream-lake interactions.

2.2.2. Synoptic Sampling Design

To date, research informing ecosystem change on the North Slope of Alaska has been based on either small (i.e., point or plot scale) or large (i.e., regional or pan-Arctic) field and modeling studies (Metcalfe et al., 2018). Further, spatially extensive studies that include samples taken at the inflow and outflow of lakes are limited in this region. To answer question 1, I leverage extant "synoptic" water chemistry data from 29 sample locations that were collected throughout Oksrukuyik Creek watershed (Shogren et al., 2021; Abbott, 2021).

Stream water samples were collected in August 2016, and then twice (June and August) each thaw season in 2017 and 2018. Each synoptic sampling event consists of 1L water grab

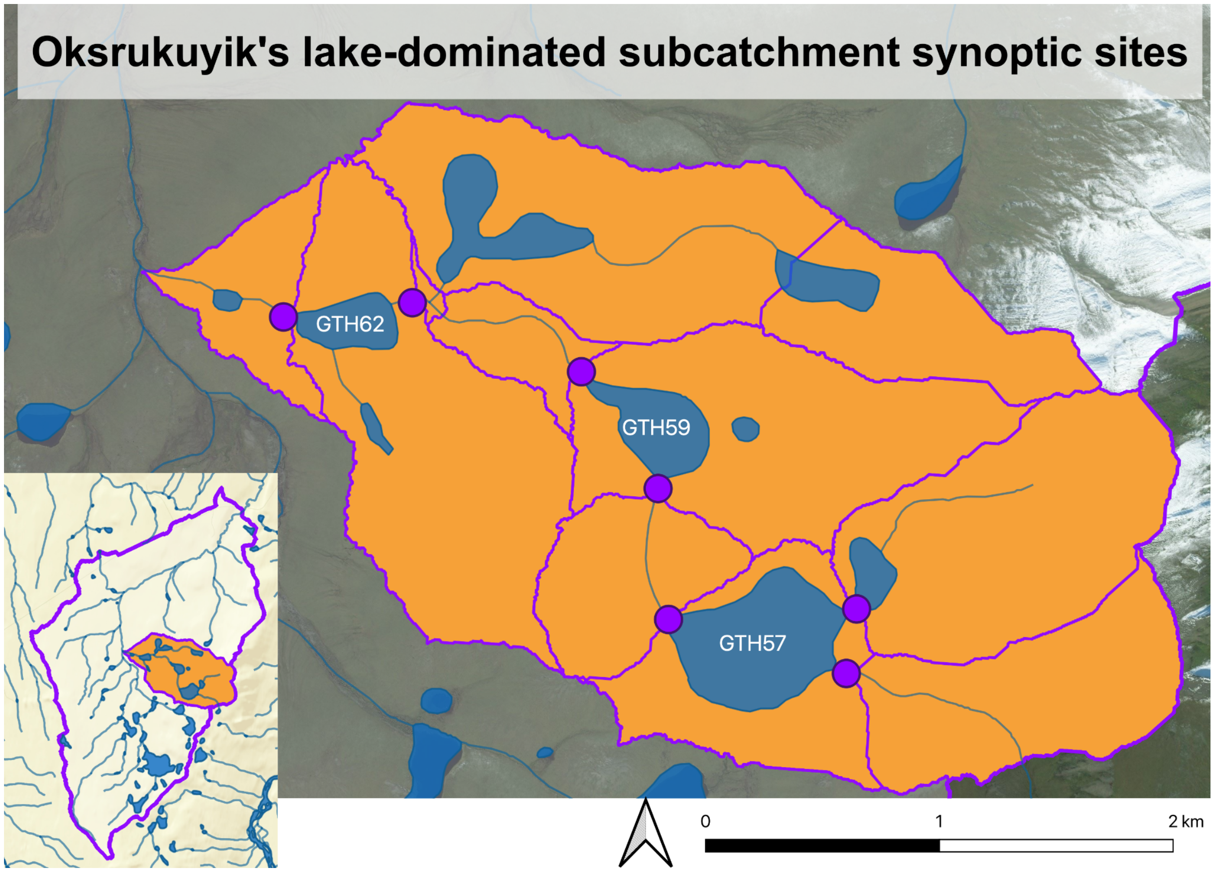

Figure 2.2.2: The three lake names, location along the river network and synoptic sampling sites within Oksrukuyik Creek watershed lake-dominated subcatchment.

samples taken over the course of 5-6 hours throughout the watershed. At each site, dissolved oxygen (DO), specific conductance, pH, and temperature were measured in the field using a handheld YSI Pro DO multiparameter probe (YSI Instruments Part No: 626281). In addition, this dataset includes a wide range of water chemistry data including dissolved organic carbon (DOC), nitrogen species (nitrate [NO_3^-], ammonium [NH_4^+], dissolved organic nitrogen [DON], and total dissolved nitrogen [TDN]), phosphorus species (total dissolved phosphorus [TDP], and soluble reactive phosphorus [SRP]), as well as numerous other solutes including sulfate, chloride, iron, silicon, and calcium.

Table 2: Analytical methods for solute analysis					
Instrument used in analysis	Total Carbon Analyzer (Shimadzu TOC-L$_{CPH}$; accuracy +/- 5%)	Quikchem Flow Injection Analysis System (Lachat, accuracy +/- 2.5%)	Spectrophotometer (Shimadzu UV-2600, accuracy +/- 0.3%) (Parsons et al., 1984).	Integrated Ion Chromatography (IC) System (Dionex ICS-2100, Thermo Scientific, Waltham, U.S.A.)	Inductively Coupled Plasma (ICP) Spectrometry (iCAP 7000 series, Thermo Scientific, Waltham, U.S.A.)
Parameter(s)	DOC, TDN	NO_3^-, NH_4^+	SRP, TDP, PO_4^{3-}	Acetate, formate, Br, Ca, Cl, Li, NO_2^-, SO_4^{2-}	Al, As, B, Ba, C, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sr, Ti, V, Zn

In the field, grab samples were collected in acid-washed 1 L amber PCTE bottles. Samples were filtered in the lab for specific carbon analytes within 8 hours of collection. Each sample was filtered with a syringe filter (25 mm, 0.7 µm nominal pore size GF/F, Whatman) into pre-rinsed dark (DOC) and clear (all other solutes) 60mL bottles. Samples were frozen (-4 ºC) until analysis, with the exception of DOC aliquots which were stored at 2 ºC until analysis. Frozen water samples were mailed to Brigham Young University (BYU) and University of Vermont (UVM) for water chemistry analysis (Table 2).

2.2.3. Estimation of Lake Residence Time

Generally, lack of lake inflow and bathymetry data limits our ability to accurately estimate lake residence time in this region of the Arctic. Therefore, to calculate lake residence time for Oksrukuyik Creek study lakes, I used previously estimated measurements of stream inflow discharge (L s^{-1}), known lake volume (L) (Stuckey et al., 2019), and delineated subcatchment area (km^2). Subcatchment delineation began using coordinates from sampling locations as starting points and importing them into a GIS (ESRI ArcGIS v.10.4). Subcatchment area was delineated using the Hydrology toolset within the Spatial Analyst toolbox and the following two digital elevation models (DEMs): ArcticDEM from the Polar Geospatial Center (Porter et al., 2018) and ASTER GDEM v.2 (NASA/METI/AIST/Japan Spacesystems and US/Japan ASTER Science Team, 2009). This watershed delineation method was conducted for all sampling locations through a Python script to calculate upstream subcatchment area (Shogren et al., 2021).

The discharge ($L\ s^{-1}$) was measured twice at selected sites in the Oksrukuyik watershed (n = 8 of 42 synoptic sites) in June and August of 2019 using salt dilution gauging (Hongve, 1987). I used these discharge measurements to estimate the inflows to the ungauged lakes included in my study. This approach assumes that runoff generated within the 8 selected synoptic sites is representative of the runoff volumes generated across the entire watershed, a reasonable assumption considering the minimal variability in the subsurface storage of water due to permafrost. To estimate the lake inflows, I converted the measured discharges to specific discharge at each site by dividing discharge by watershed area of the stream location (km^2), giving units of $L\ km^{-2}\ s^{-1}$. I then used the mean of the measured specific discharges in the watershed to estimate the discharge at the lake inflow sites given their known subcatchment areas. I did this estimation of lake inflows for both the early and late season conditions. Next, I used the published lake volumes (Toolik Field Station GIS, 2013; Toolik Field Station GIS, 2015a & 2015b) to approximate lake residence time by dividing lake volume by estimated inflow discharge. This resulted in an instantaneous mean residence time of water in each lake for early and late season.

2.2.4. Statistical Analyses

For question one, to determine how subcatchments with varying lake influence modulate biogeochemical solutes, I compared the spatial stability of all three subcatchment categories from Oksrukuyik Creek with varying lake influence (low, medium, and high lake influence). Spatial stability refers to the subcatchment's solute source and transportation stability through time. A spatial stability metric provides insight into whether solute conditions are stable at a specific location (i.e., do not reshuffle but can change positively or negatively), or if the conditions and controls on the solute are changing through time (i.e., solutes shuffle and subcatchment is spatially unstable) (Figure 2.2.3.A). The spatial stability metric specifies the temporal stability of a subcatchment's spatial patterns by using Spearman's correlation which quantifies stability (Abbott et al., 2018; Shogren et al., 2019; Shogren et al., 2021). Spearman's rank correlation coefficient (r_s) calculates the monotonic relationship between rank values of two variables: solute concentrations during early season (June) and late season (August). The result is a single r_s value, ranging between +/- 1 that describes the correlation and dependence of one

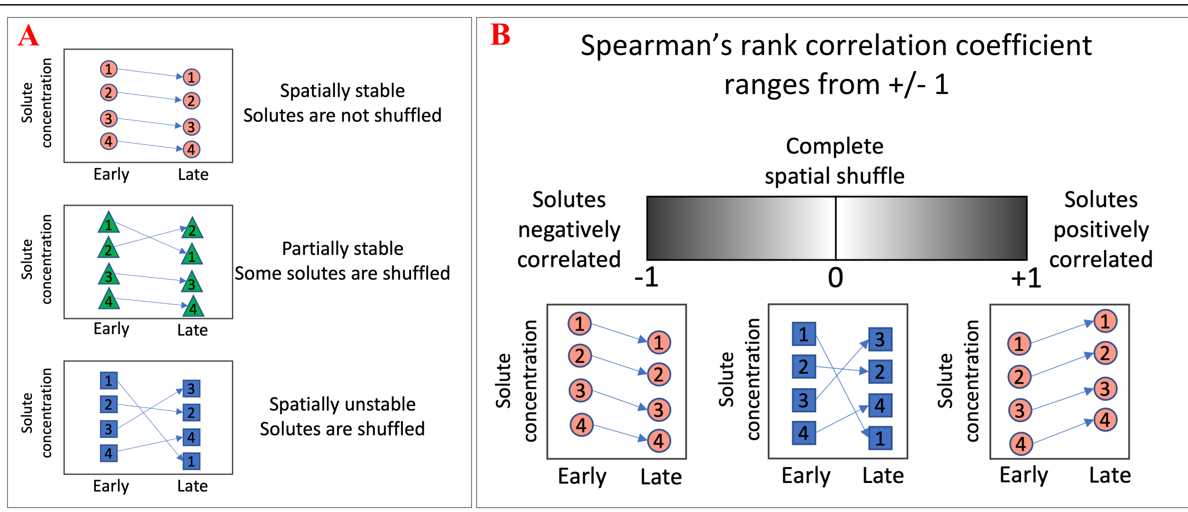

Figure 2.2.3: Visual representation of subcatchment spatial stability and calculated metric. Description of each is as follows: A) Visual range of subcatchment spatial stability from stable to unstable based on solute concentrations in early thaw season versus late thaw season, and B) Spearman's rank correlation coefficient range and reciprocating spatial stability visualization.

variable to the other. An $r_s \approx +1$ indicates the spatial arrangement of solutes were spatially stable with a positive correlation over the thaw season, an $r_s \approx -1$ indicates the spatial arrangement of solutes were spatially stable with a negative correlation over the thaw season and $r_s \approx 0$ indicates the spatial arrangement of solutes was spatially unstable over the thaw season (Figure 2.2.3.B). A t-test is calculated to determine the significance level of the correlation between early and late season solute concentrations. Significance is indicated by a probability (p value) less than alpha = 0.05.

For question two, to assess how lake size and residence time modulates (removes/produces) lake solute chemistry, I conducted ANOVA tests comparing the inflow to outflow solute concentrations of three lakes in the lake dominated subcatchment of Oksrukuyik Creek watershed. Further, I separate inflow and outflow concentrations based on seasonal effects (June/August) and conduct t-tests/ANOVA to determine if seasonality influences lake nutrient processing. Finally, I calculate fluxes by multiplying concentration by discharge (L s^{-1}) for both the outflow and inflow during the early and late season. I then compare the difference between outflow and inflow total flux based on season and run ANOVA to determine if the change in total flux is dependent on the season (i.e., early versus late thaw season).

2.3. Results

2.3.1. Influence of Subcatchments with Varying Stream-Lake Interactions

Overall, increasing lake influence in the river network increases the spatial instability of solutes when comparing early and late thaw season conditions. In general, the lake dominated (high-lake influence) subcatchment was the most unstable for nearly all solutes (r_s<0.5), with the exception of two stable solutes: NH_4^+ (r_s = 0.69, p-value = 0.02) and Fe (r_s = 0.6, p-value =

0.056). The mid-lake influence watershed showed solute stability for four out the fourteen solutes: TDN (r_s = 0.7, p-value = 0.00078), NO_3^- (r_s = 0.54, p-value = 0.015), DON (r_s = 0.76, p-value = 0.00014), and Na (r_s = -0.65, p-value = 0.049). Finally, the subcatchment with low-lake influence was the most stable with seven out of fourteen solutes being stable: DOC (r_s = 0.74, p-value = 0.0024), NO_3^- (r_s = 0.57, p-value = 0.035), DON (r_s = 0.63, p-value = 0.019), SO_4^{2-} (r_s = 0.98, p-value = 0.0004), Cl (r_s = 0.74, p-value = 0.046), Ca (r_s = 0.96, p-value = 0.0002), and Fe (r_s = 0.9, p-value = 0.0046). Additionally, the high-lake influenced subcatchment had only one

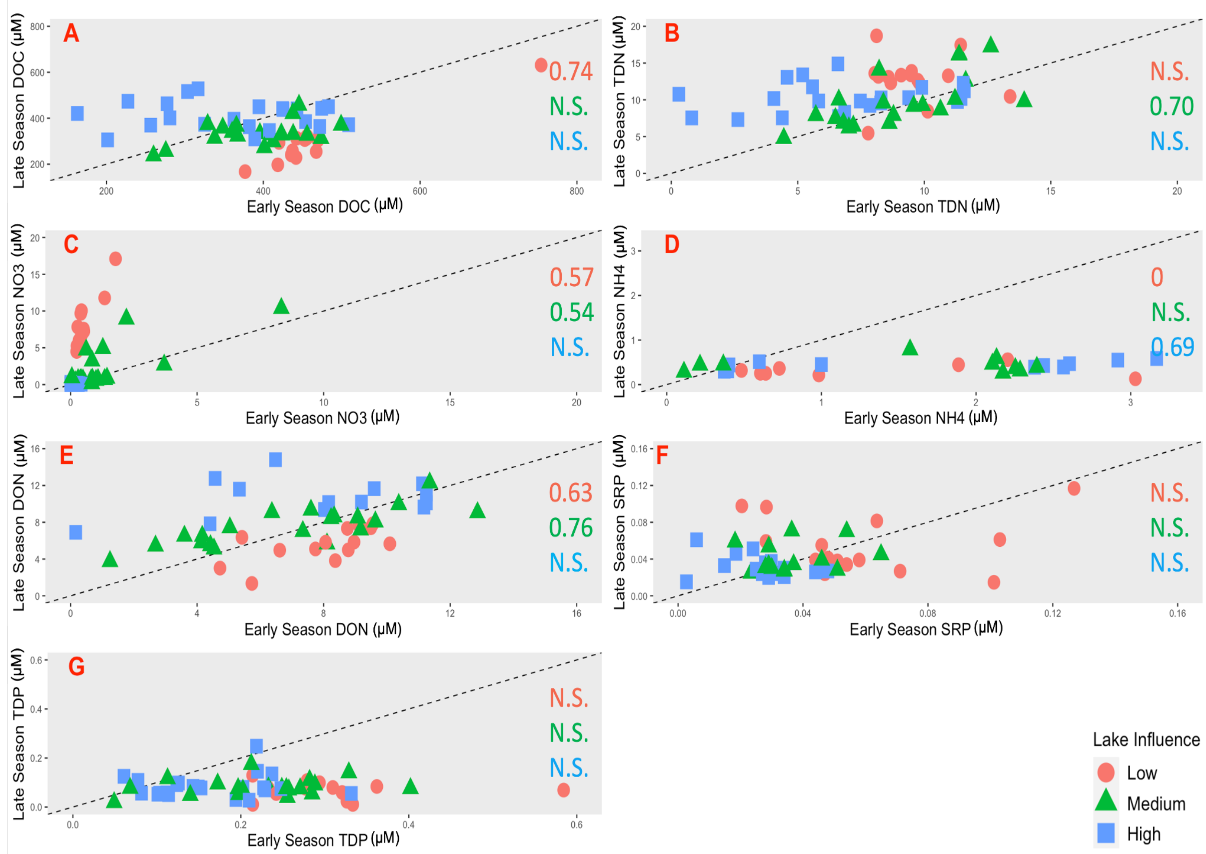

Figure 2.3.1: Seasonal stability of inorganic and organic nutrient solutes for three subcatchments of Oksrukuyik Creek watershed: low-lake influence (pink circles), medium-lake influence (green triangles), and high-lake influence (blue squares). The 1:1 line on the concentration plots indicate no seasonal shift, whereas points above the line increase from early to late season, and points below the line decrease from early to late season. Also, the significant rank correlation coefficients (r_s) are shown on each plot for solutes that were calculated to have p-values < 0.05), otherwise "N.S." is reported for p-values greater than 0.05.

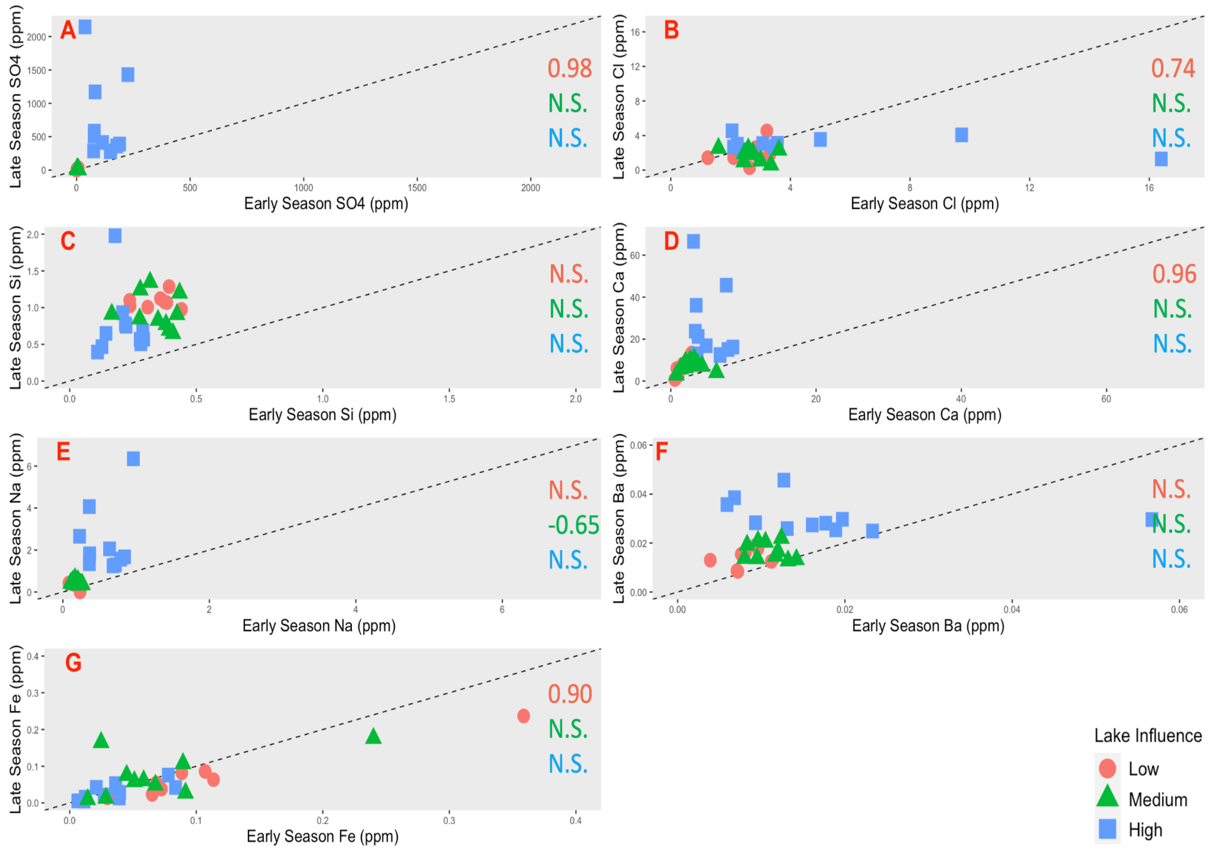

Figure 2.3.2: Seasonal stability of dissolved anions and cations for three subcatchments of Oksrukuyik Creek watershed: low-lake influence (pink circles), medium-lake influence (green triangles), and high-lake influence (blue squares). The 1:1 line on the concentration plots indicate no seasonal shift, whereas points above the line increase from early to late season, and points below the line decrease from early to late season. Also, the significant rank correlation coefficients (r_s) are shown on each plot for solutes that were calculated to have p-values < 0.05), otherwise "N.S." is reported for p-values greater than 0.05.

stable solute (NH_4; p-value = 0.02; Figure 2.3.1.D), while all solutes were stable in the mid- and no-lake influenced subcatchments (Figure 2.3.1 & Figure 2.3.2).

A few solute patterns of interest also emerged. DOC and NO_3^- decreased in stability 0.74), with low stability in mid-lake influence (r_s = 0.26) and no stability in high-lake influence (r_s = -0.05) subcatchment. NO_3^- stability ranged from r_s = 0.57 in the low-lake, r_s = 0.54 in the mid-lake, to r_s = 0.15 in the high-lake subcatchment. SRP had the opposite pattern, where the high-lake influence subcatchment was more stable (r_s = -0.30) than the less lake influenced subcatchments (mid-lake r_s = 0.24, low-lake r_s = -0.17). With increasing lake influence, there was also a decrease in organic solute stability. Within the low-lake influence subcatchment, DOC and DON were stable spatially. In the mid-lake influence subcatchment, only DON was stable. Finally, in the high-lake influence subcatchment, no organic solutes were stable. DOC was only stable within the low-lake influence subcatchment (r_s = 0.74), and significantly decreased in stability with increasing lake influence (mid-lake r_s = 0.26, high-lake r_s = -0.05). This decrease in stability signifies unstable DOC processing within the lakes through the thaw season.

2.3.2. Influence of Lake Residence Time within a Lake-Dominated Subcatchment

Mean lake residence times varied on the order of days to years between three different lakes in the lake-dominated subcatchment of Oksrukuyik Creek. Based on mean specific discharge calculations between early and late thaw season (Early = 85.4 L km^{-2} s^{-1}; Late = 37.7 L km^{-2} s^{-1}), the residence time of the smallest volume lake (GTH62; $1.79*10^8$ L) ranged from 17-40 days, the medium volume lake (GTH59; $7.62*10^8$ L) ranged between 3-6.5 months, and the largest lake (GTH57; $3.82*10^9$ L) ranged from 2-4 years, with longer residence times in the late thaw seasons or when stream inflows were small. For reference and figures, different residence times are labelled with a characteristic residence time of days, months, or years (Table 3). The longest residence time lake (GTH57; τ = years) is located in the headwaters of the lake-

Table 3: Calculated and characteristic residence time for lakes in Oksrukuyik Creek lake-dominated subcatchment

Lake	Volume (L)	Residence Time [τ] Range (years)	Characteristic Residence Time
GTH62	1.8E+08	0.05-0.1	Days
GTH59	7.6E+08	0.25-0.5	Months
GTH57	3.8E+09	2-4	Years

dominated subcatchment, where cumulative subcatchment area (km^2) and stream inflow are the smallest. The next lake along the river network has a residence time of months (GTH59; τ = months). The smallest lake is located furthest downstream, immediately upstream of the Oksrukuyik Creek mainstem and has the shortest residence time (GTH62; τ = days) (Figure 2.2.3).

By separating the inflow and outflow concentrations for the individual lakes, I determined if residence time impacts the ability of a lake to modulate biogeochemical signals

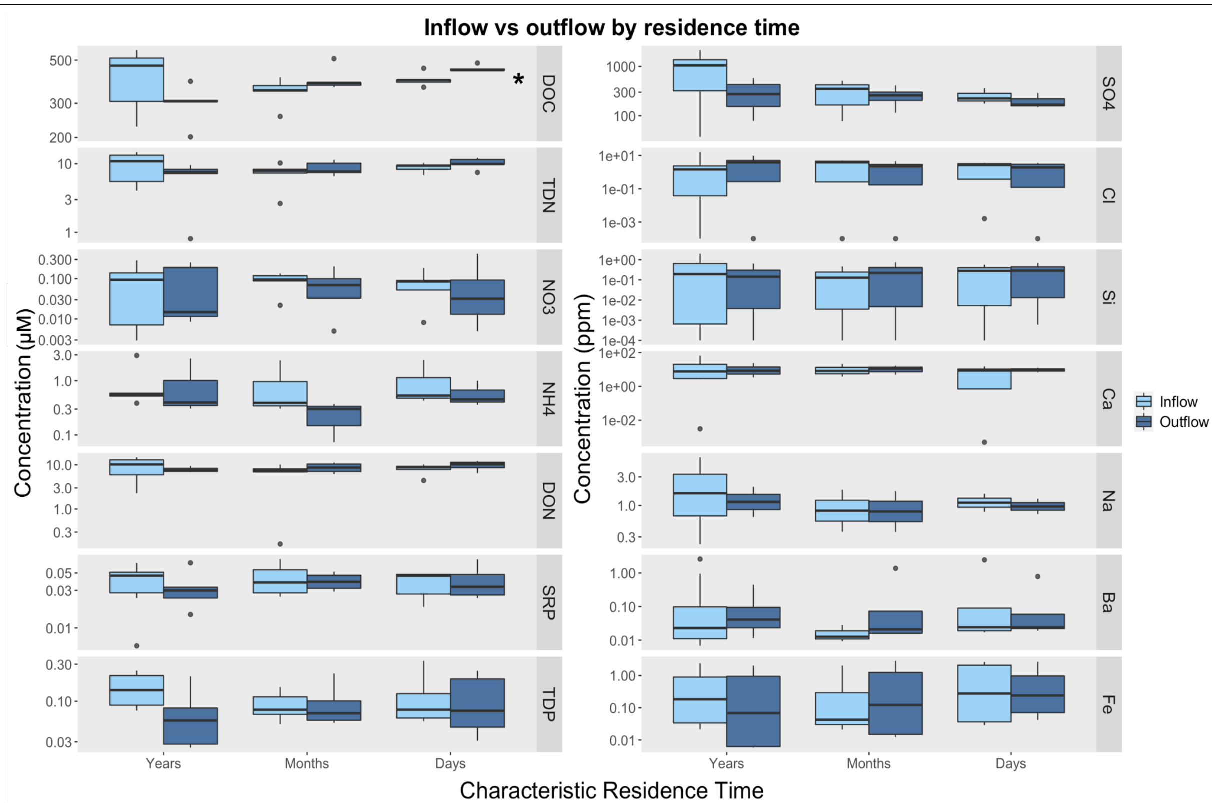

Figure 2.3.3: Boxplots for each lake of varying characteristic residence times (Years/Months/Days) comparing their respective inflow (light blue) and outflow (dark blue) solute concentrations over an entire thaw season for all three years of data. Note: the left panel solutes are reported in μM, and right panel solutes are reported in ppm. Y-axis concentration ranges are unique to each solute. Boxplots indicate the median concentration value with the solid black horizontal line and the lower and upper hinges (the 25th and 75th percentiles) are shown with colored boxes. Whiskers extend to 1.5*IQR (interquartile range), and any points beyond are outliers. Asterisks present next to the boxplots indicate significant difference in solute concentrations based on ANOVA tests (p-value<0.05 [*], p-value<0.01[**], p-value<0.001 [***]).

over the course of a thaw season. Based on ANOVA tests, the only significant difference in concentration between the inflow and outflow occurred on the smallest lake with a residence time of days and for one solute (DOC; p-value = 0.014). For all three lakes, all other solutes were not significantly different between the inflow and outflow (p-value > 0.05) (Figure 2.3.3). While ANOVA results show the majority of solutes were not significantly different, the range and values of certain solute concentrations shifted after lake influence. For example, the largest lake that had a residence time of years had outflowing biogeochemical signals that decreased overall or had dampened variability for DOC, TDN, DON, and TDP, as did the medium sized lake with a residence time of months for outflowing NH_4^+.

Although the aggregated multi-year biogeochemical signals did not significantly change between the inflow and outflow when assessed over the entire thaw season, there was a change in the biogeochemical signals between the inflow and outflow when differentiating between the early and late thaw season solute concentrations. Based on ANOVA tests, the largest lake acted as a solute sink during the late thaw season for three solutes: DOC (p-value < 0.001), TDN (p-value = 0.0037), and DON (p-value = 0.017), and was a solute source for Cl (p-value = 0.019) (τ = years; Figure 2.3.4). Additionally, the lake with the longest residence time showed marginally significant differences (p-value < 0.1) for an additional three solutes (NH_4^+, TDP, and SO_4^{2-}), and thus there is evidence for significant modulation of seven out of the 14 solutes during late thaw season. This modulation capacity sharply decreases at the lake with month-long residence time, where there are no solutes with a significant variation, and at the lake with day-long residence time, where DOC is the only significantly modified solute (p-value < 0.001). Early thaw season ANOVA results showed no significant modulation of solutes for any lake (p-value > 0.05).

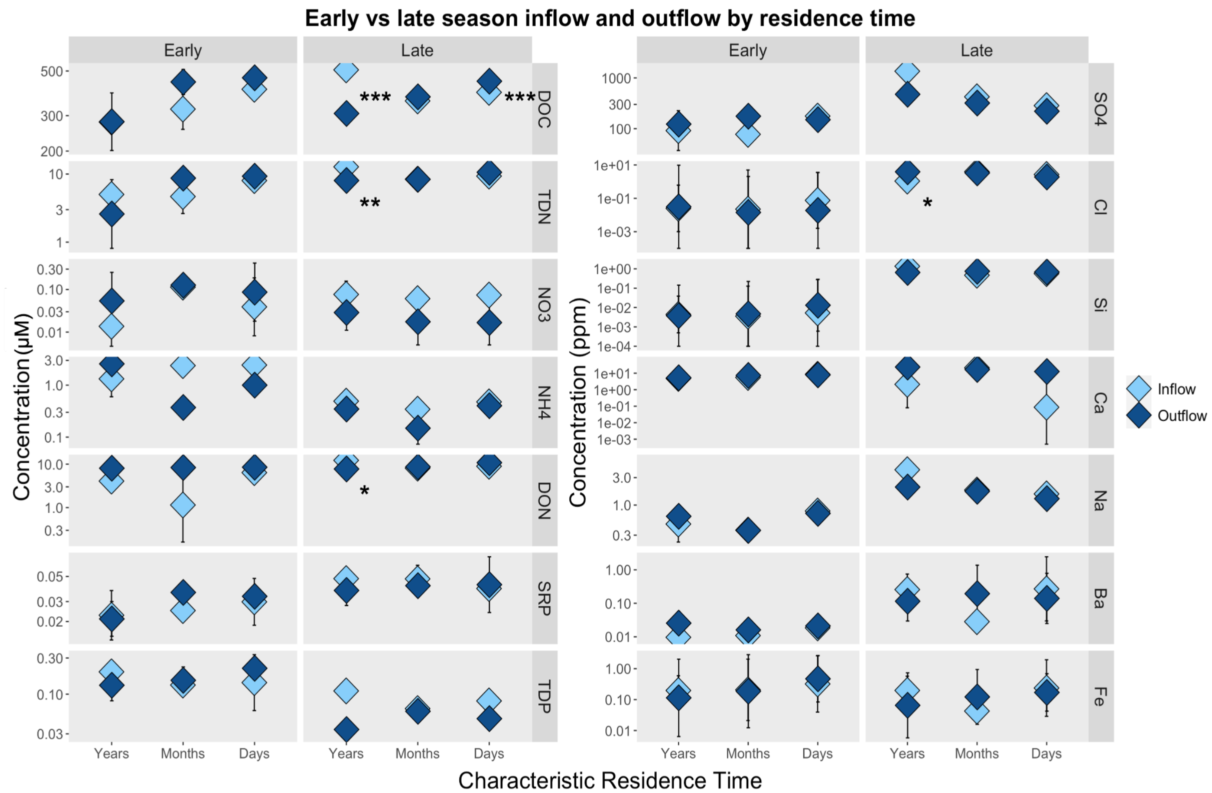

Figure 2.3.4: Means and standard errors of solute concentrations at the inflow (light blue) and outflow (dark blue) for each lake of varying residence times (Years/Months/Days) during early and late thaw season. The left panel solutes are reported in µM, and right panel solutes are reported in ppm. Y-axis concentration ranges are unique to each solute. Diamonds indicate the mean concentration, and whiskers indicate standard errors. Asterisks present next to diamonds with significant difference in solute concentrations based on ANOVA tests (p-value<0.05 [*], p-value<0.01[**], p-value<0.001 [***]).

Finally, I compared the change in total flux between the inflow and outflow to distinguish lake solute production or removal during early and late thaw season. This indicates the magnitude of solute production or removal from the lake, which is meaningful for assessing watershed scale impacts of stream-lake interactions on biogeochemical budgets. ANOVA test results indicate the year-long residence time lake changed between early and late season for total flux of NH_4^+ (p-value = 0.006) and Si (p-value = 0.015). The month-long residence time lake changed for DOC (p-value = 0.0004), TDN (p-value = 0.0011), NH_4^+ (p-value = 0.031), and DON (p-value = 0.007). Finally, the day-long residence time lake changed for DOC (p-value =

0.011), and NH_4^+ (p-value = 0.043) (Figure 2.3.5). Late season total change in flux was consistently buffered (flux ≈ 0) for the majority of solutes. In comparison, early season had greater differential effects on total flux, which also tends to have a more extreme lake flux response at the month or day residence time lakes (e.g., Figure 2.3.5: DOC, TDN, NO_3^-, NH_4^+, DON, SRP, TDP, Cl, Ca, and Fe). While the late thaw season trend is often buffered, there are a few exceptions. The longest residence time lake had four solutes whose change in flux was higher in the late season: SO_4^{2-}, Si, Na, and Ba. In the month-long residence time lake, two solutes had larger change in flux in the late season: Si and Na, while the day-long residence time lake showed greater change in flux for Si and Ba. Si was the common solute whose change in

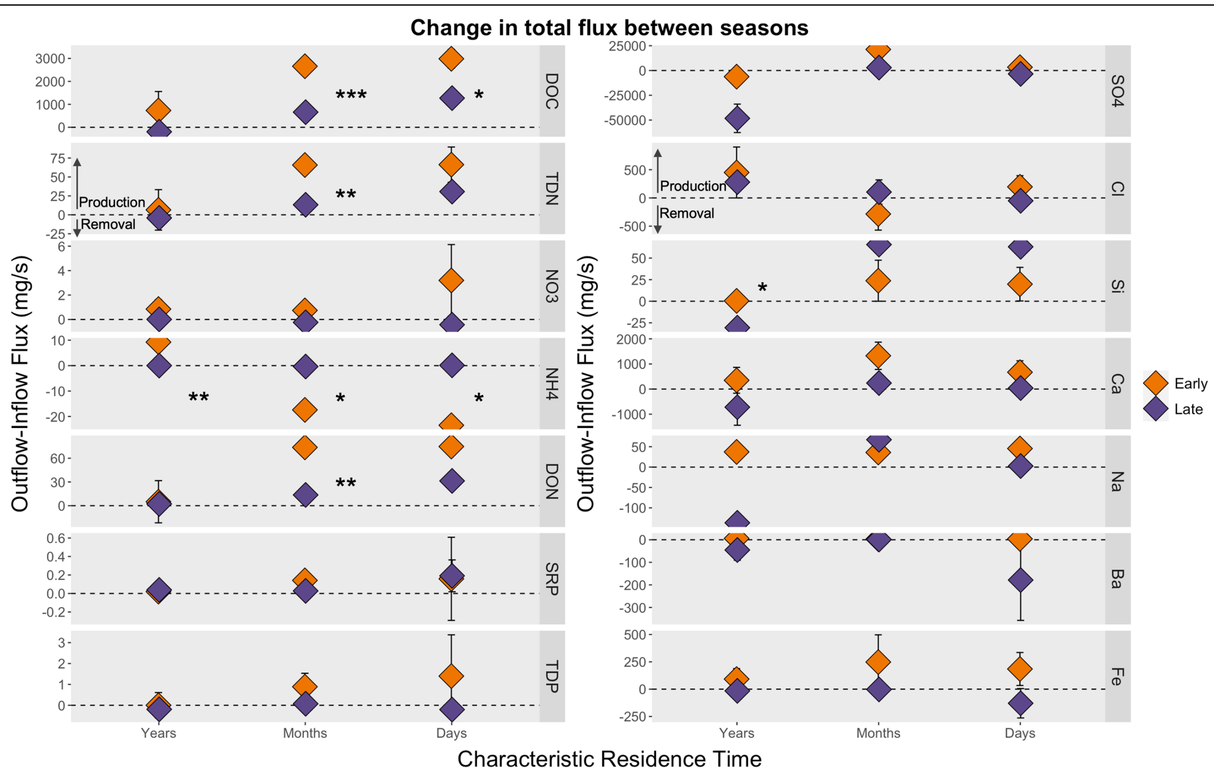

Figure 2.3.5: Means and standard errors of total solute flux change (outflow-inflow flux) during early thaw season (orange) and late thaw season (purple) for each lake of varying characteristic residence times (Years/Months/Days). The black dashed line indicates no change in flux. Above the dashed line indicates solute production, and below the dashed line indicates solute removal. Y-axis concentration ranges are unique to each solute. Diamonds indicate the mean concentration, and whiskers indicate standard error. Asterisks present next to diamonds with significant difference in solute concentrations based on ANOVA tests (p-value<0.05 [*], p-value<0.01[**], p-value<0.001 [***]).

flux was larger in the late season than the early season across the three lakes. Nevertheless, the overall trend for most solutes, especially the nutrients, was that lakes buffer biogeochemical signals more significantly in the late season than early thaw season.

2.4. Discussion and Conclusion

In all, using solute concentration spatial patterns and inflow vs outflow solute fluxes to compare lake residence time and seasonality provided some insights into the different capacities of lakes to modulate biogeochemical signals. These spatial results show lakes with longer residence time within Oksrukuyik Creek's lake-dominated subcatchment modulated biogeochemical signals in inconsistent and variable ways. To understand how stream-lake interactions modulate biogeochemical signals in a river network, it may be necessary to analyze how residence time and seasonality interact with the lake dynamics and processes.

2.4.1. The Role of Stream-Lake Interactions in Modulating Riverine Biogeochemistry

River networks that have lake influence in the Arctic, like other better studied temperate regions, may modulate nutrients in a variable and inconsistent way. My research demonstrates that the extent of this modulation effect likely depends on the level of stream-lake interactions present. Subcatchments with less lake influence were found to be more spatially stable and less variable in solute concentrations than subcatchments with lake influence.

In this study, there was a shift in the total number of stable solutes in each subcatchment, and solute stability showed a negative correlation with increasing stream-lake interaction. In a previous study, the biogeochemical conditions of Oksrukuyik Creek watershed were compared to nearby watersheds, including watersheds with little to no lake influence (Shogren et al., 2019).

That study did not focus on stream-lake interactions, but it did show that Oksrukuyik Creek watershed had low spatial stability for DOC and NO_3^- compared to the nearby alpine and tundra watersheds with little to no lakes present. Also, in Shogren et al. (2019), the SRP in Oksrukuyik Creek had the highest spatial stability in late thaw season (August), which was attributed to an increase in mineralization along deeper soil horizons later in the thaw season (Harms and Jones, 2012; Shogren et al., 2019). Here, my detailed analysis of Oksrukuyik Creek subcatchments supports an interpretation that at the landscape scale the presence and abundance of lakes are controls on river network DOC and NO_3^-. Additionally, their SRP findings directly align with the results found in this study that focused on subcatchments within Oksrukuyik Creek watershed with varying stream-lake interactions showing that there was not a strong lake effect on SRP and therefore is likely a more diffuse control like mineralization along soil flow paths to the stream network.

Furthermore, there was a general shift of stable inorganic solutes within the high-lake influence subcatchment to more stable organic solutes in the low-lake influence subcatchment which also indicates there may be a larger lake effect on inorganic solutes (i.e., through mineralization and nutrient processing within the high-lake influence subcatchment on inorganic solutes) and that this inorganic nutrient effect is less clearly observed when stream-lake interactions decrease. However, attributing specific process-based controls on these patterns is not possible given the study design because during the late thaw season, both landscape water and material sourcing changes as do internal lake conditions. These concurrent shifts make it hard to specify specific solute controls when there is only information within the stream channels and not within the hillslopes or within the lakes. For example, active layer thaw depth increases in the hillslopes through the thaw season and pools of organic solutes are mobilized into aquatic systems as water flow paths can reach deeper soil organic layers (Petrone et al., 2006; Harms and Jones, 2012). Additionally, the late thaw season alters Arctic lake dynamics by increasing the lake's thermal stratification depth, mixing, and processing (MacIntyre et al., 2009), therefore increasing solute mineralization potential (Wetzel 2001; Cantin et al., 2011; Fortino et al., 2014). Hence, the specifics of solute stability control locations and processes are not ascertainable in this study, but there is clear evidence in the stability metrics that stream-lake interactions and seasonality play a role in the spatial patterns of biogeochemistry in Oksrukuyik Creek.

2.4.2. Importance of Lake Residence Time

In this study, I found lake size is positively correlated with lake residence time within the lake-dominated subcatchment of Oksrukuyik Creek watershed. Lake residence time was also dependent on the season, where residence time doubled from the early to late thaw season due to changes in the lake inflow rates. Other studies have found Arctic lake's residence time changes from shorter residence time in the early season to longer residence times in the late season, mostly due to increased evaporation after ice-off and decreased runoff rates later in the thaw season (Thomas et al., 2020). Within Oksrukuyik Creek's lake-dominated subcatchment, runoff in the early thaw season is dominated by a combination of snowmelt and precipitation events. This shifts in the late season where runoff is dominated by precipitation events and continued active layer thawing (Shogren et al., 2020b). The general increase in lake residence time during the late thaw season is largely influenced by decreased stream specific discharge of the streams and increased lake evaporation.

Previous studies have shown residence time has a positive relationship with internal lake processing and heterotrophy (Kling et al., 2000; Zwart et al., 2017). While inflow solute concentrations were not significantly different at the outflow between varying residence time lakes in Oksrukuyik Creek watershed, results from this study showed that certain solute concentrations shifted after lake influence. Solute concentrations decreased or dampened at the outlet in the year-long residence time lake for four solutes (DOC, TDN, DON, and TDP), as well as the outflow of the month-long residence time lake for NH_4^+, indicating longer residence time may have higher processing potential for certain solutes. Yet, more data are required to determine if the solute dampening signal is related to lake heterotrophy.

Seasonality plays an important role in how solutes are processed in the hillslope and lake system. Seasonality again has an interaction with the lake residence time relationships with solute conditions. During late thaw season within the lake-dominated subcatchment, the lake with the longest residence time modulated four solutes (DOC, TDN, DON, and Cl), as compared to no solute modulation in the medium and modulation of just one solute (DOC) in the low residence time lakes within the same subcatchment. During the early thaw season, no solutes in any lake were significantly modulated (p-value > 0.05; Figure 2.3.4).

My research provides insights into the timing and magnitude of when an Arctic lake is a solute source (production) or sink (removal) between the early and late thaw season. The late season buffering effect was demonstrated when comparing early thaw season total flux to late thaw season total flux. Solute total flux was relatively modulated (flux ≈ 0) during late season sampling for the majority of sampled solutes, with the exception of Si in all three lakes, and SO_4^{2-}, Na and Ba inconsistently in the three lakes. This result is supported by a study in the nearby Toolik Lake, whose volume is an order of magnitude larger than the largest lake in this study (GTH57) and therefore may have a larger processing potential. This Toolik Lake study found that dissolved reactive silicon (DRS) was produced in the lake during the early thaw season and switched to DRS removal in the late season (Cornwell and Banahan, 1992). The late season DRS removal was attributed to sedimentation. These results could provide a basis for understanding when and where silicon is processed in Arctic lakes. Silicon in the year-long residence time lake from our study showed removal in the late season, whereas change in the early season was negligible. This relationship switched in the month and day-long residence time lakes when silicon was produced to a larger degree in the late season than the early season. Another switch occurred with NH_4^+ in the early season, when the lake with year-long residence time showed NH_4^+ production, then removal in the month and day-long residence time lakes. Meanwhile, late season NH_4^+ was negligible, yet significantly different from early season NH_4^+ (p-value < 0.05). A study found NH_4^+ switches between produced within lakes and consumed within streams (Kling et al., 2000). The findings from Kling et al. 2000, and results from this study may indicate NH_4^+ has a threshold for processing potential at specific residence times. The month and day long residence time lakes are acting more "stream-like" than the year-long residence time lake. While the specific controls on NH_4^+ in the early thaw season are still not clear, this may be an area for future studies to determine the role of residence time and seasonality on NH_4^+ processing.

2.4.3. Study Limitations and Future Directions

There are several limitations with the current study and opportunities for future studies assessing stream-lake interaction effects on watershed biogeochemistry. Below I describe two such limitation and how they may influence the interpretation of my results. First, instantaneous discharge was collected only twice during the thaw season and never directly at the inflow or outflow of the study lakes within the lake-dominated subcatchment. Since repeated and inflow/outflow sampling was not possible, we made a general continuous discharge assumption to estimate residence time for this study. This sampling approach limits the accuracy of and introduces uncertainty into the lake residence time calculations.

Second, we assumed that residence time is a proxy for biogeochemical processing potential. Although this assumption is often applied in lake studies when internal lake data is limited (Zwart et al., 2017), it ignores that hydrodynamics may create more complex internal mixing of waters that is not well characterized by an instantaneous mean residence time. For example, the individual lake beds, wave action, thermal stratification, and water currents are not likely uniform throughout the Oksrukuyik lakes and water residence time should appear more as a distribution of times within the lake and its outlet at any point in time (Monsen et al., 2002). Future studies could develop a hydrodynamic model, similar to Monsen et al (2002), or make direct measurements of stratification and spatial biogeochemical heterogeneity. This would help determine the spatial and temporal residence time variability within each lake and assess the range of biogeochemical processing within Oksrukuyik lakes.

While the results of this study concur with the few previous studies of watershed scale stream biogeochemistry, it is important to continue collecting synoptic samples within the Oksrukuyik Creek watershed as the annual range in the present study is limited, spanning only two years, and long-term synoptic data sets are extremely rare yet valuable wherever they exist in the world (Abbott et al., 2018). Additionally, incorporating additional solutes and the ratios of geogenic solutes (i.e., Strontium isotopes, Ca/Na, Ca/Ba, and Fe/P) into this analysis may provide more insight into lake solute dynamics, biogeochemical modulation, and sourcing of solutes going into and out of the lake (Keller et al., 2010; Herndon et al., 2019). Collecting information about the ecological conditions and conducting biogeochemical experiments within the lakes of Oksrukuyik Creek may also help identify specific processes controlling individual solutes and confirm or refute the above interpretations about how lakes serve as a source or sink of specific solutes at the watershed scale (Shogren et al., 2019). For example, one could set up a study that has more focus on a gradient of residence times in Oksrukuyik lakes, so you have more than three sites and more resolution instead of days, months, years or at least a better representation of characteristic residence time of lake water (i.e., more than n = 1). Future studies can also measure lake metabolism and analyze C and N budgets in the lakes to determine if lake conditions are advantageous for mineralization of organic solutes and where within lake source and sinks of biogeochemical inputs are occurring.

2.4.4. Conclusion and Broader Implications

Studies of the effect of stream-lake interactions in temperate systems have indicated that lakes modulate biogeochemical signals (Goodman et al., 2011; Baker et al., 2016). My study showed stream-lake interactions in the Arctic, an understudied aquatic system, also act as both sources or sinks of aquatic nutrients and vary over an Arctic thaw season. Stream-lake interactions, lake properties, and seasonality in water chemistry are rarely, if ever, assessed in most landscape scale ecosystem or watershed budget studies of biogeochemical conditions in the Arctic (Shogren et al., 2020a), so expanding analyses of these stream-lake interaction factors is an open area of research.

This study also revealed that how individual lakes modulate biogeochemical signals varies among lakes within the same watershed and within each lake through time across a thaw season. The use of subcatchment spatial stability and residence time captures processes and patterns in a range of stream-lake interactions across an entire watershed, a scale rarely assessed

(Abbott et al., 2018; Shogren et al., 2019). Now, detailed field experimental and theoretical modeling studies are needed to develop process-based explanations for these stream-lake interaction patterns and effects.

With over a quarter of lakes on Earth existing in northern high latitudes (Lehner and Döll, 2004), lakes are a defining, yet understudied, component of Arctic systems and Limnology research in general. As the Arctic continues to undergo progressive warming and hydrologic intensification (Solomon et al., 2007; Rawlins et al., 2010; Bring et al., 2016), we can expect massive landscape and hydrologic changes that affect lakes and rivers (Ranasinghe et al., 2021). Thawing permafrost, increased thermokarst formations, and increased active layer thaw depth are expected to increase the flux of solutes (Petrone et al., 2006; Bowden et al., 2008; Harms and Jones, 2012; Hobbie and Kling, 2014; Koven et al. 2015), as well as the properties and distribution of lakes (e.g., lake initiation, expansion, and both gradual and catastrophic drainage) (Smith et al., 2005; Roach et al., 2013; Jones and Arp, 2015). Together, these system-wide Arctic changes will change stream-lake interactions in the Arctic, which this study, following the one by Shogren et al. (2019), has shown to modulate increasing nutrient fluxes being derived from broad scale permafrost degradation. Continued analysis of the effect of stream-lake interactions in the rapidly changing Arctic environment is therefore necessary to advance assessments of biogeochemical processes within Arctic river networks.

CHAPTER 3: HIGH-FREQUENCY TEMPORAL ASSESSMENT OF THE EFFECTS OF STREAM-LAKE INTERACTIONS ON BIOGEOCHEMICAL SIGNALS DURING STORM EVENTS

3.1. Introduction

Numerous watershed studies praise long-duration high-frequency data for their ability to capture processes and relationships and advance a deeper understanding of aquatic environments (e.g., Burns et al., 2019). Yet, due to logistical challenges of Arctic research, the temporal resolution of many Arctic watershed studies is low (i.e., weekly to monthly observations even at the best studied Arctic watersheds) (Shogren et al., 2020a). Prior work has demonstrated that storm events are expected to increase in frequency and magnitude in the Arctic, and typically increase nutrient flux into aquatic ecosystems and may account for a large fraction of annual flux (Raymond and Saiers, 2010; Rawlins et al., 2010; Bintanja et al., 2020). Additionally, most understanding of aquatic biogeochemistry is based upon studies during low to base flow conditions during the middle of the thaw season (Shogren et al., 2020). There are also longer duration intraannual changes given the strong Arctic seasonality and growth in progressive active layer thaw depth early through the late season alters landscape conditions (Harms and Jones, 2012; Hobbie and Kling, 2014). Therefore, I expected high-frequency solute data would reveal insights to how material during thaw season storm events is mobilized into the lake and the ability of the lake to process these new inputs during these events (Khosh et al., 2017; Connolly et al., 2018). By collecting high-frequency (e.g., every 15 minutes) discharge and solute concentration data during an entire thaw season (June-September) at the inflow and outflow of an Arctic lake, I explored the capacity of a lake to modulate solute concentrations in a stream network with unprecedented detail, with a focus on stream-lake interaction effects during multiple stream high-flow (i.e., “storm”) events.

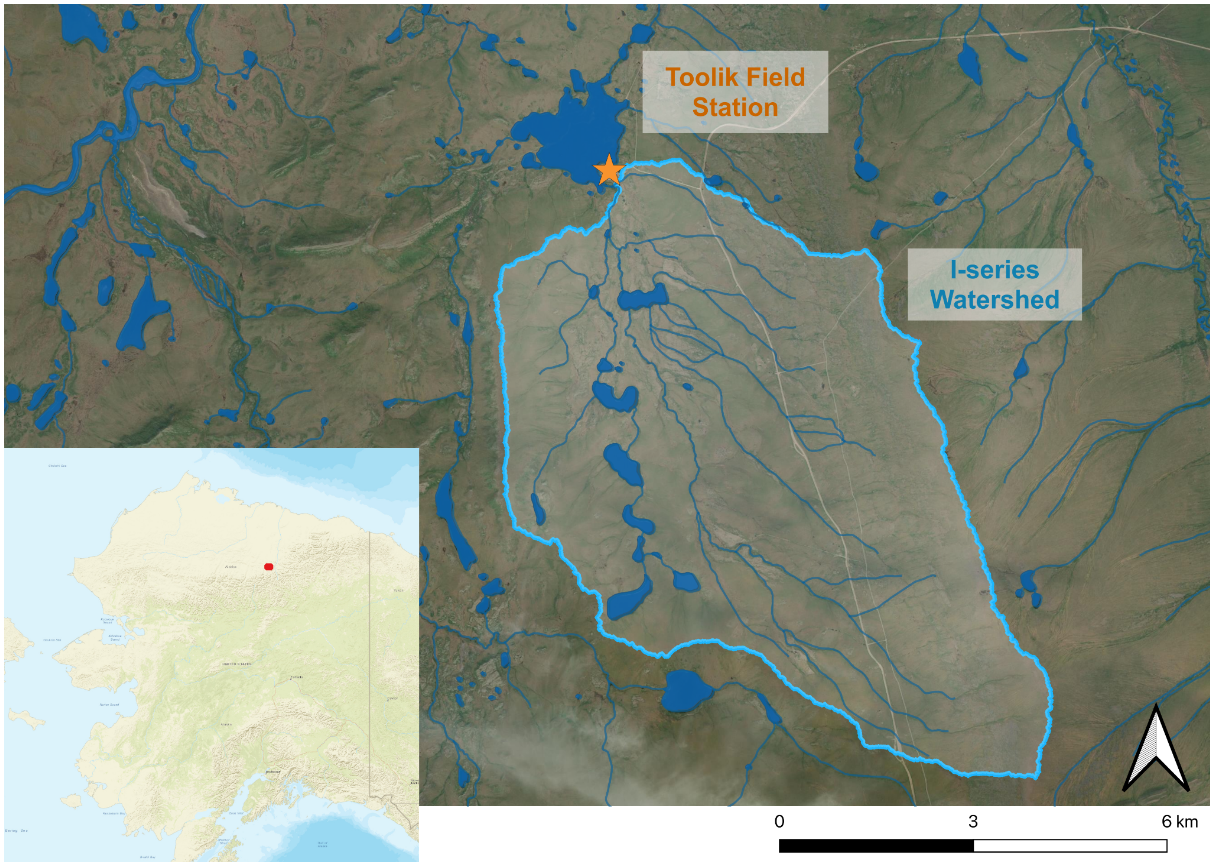

Figure 3.1.1: Site map for the I-series watershed including Toolik Field Station.

I used high-frequency stream chemistry data to examine the temporal biogeochemical dynamics during storm events, asking: 2a) How does an Arctic lake modulate the biogeochemical fluxes during storm event flows? and 2b) Do these storm event modulation effects differ between early and late thaw season when active layer, lake conditions, and terrestrial ecosystem conditions are vastly different? (Table 1). To address these questions, I specifically analyzed high-frequency dissolved organic carbon (DOC) and nitrate (NO_3^-) measurements from in situ sensors paired with discharge from the inflow and outflow of a single Arctic LTER lake (Lake I8) in the I-series watershed (Figure 3.1.1). Here I treated Lake I8 as a "black box" where within lake processes are deduced based on differences in inflow versus outflow biogeochemical signals (Figure 3.1.2 - conceptual model). And I focus on DOC and

NO_3^-. While DOC and NO_3^- are the main solutes the in-situ sensors can collect, these solutes also provide valuable information into Arctic landscape change. Export of DOC from aquatic ecosystems greatly influence the global carbon cycle, whereas NO_3^- is the major limiting nutrient in Arctic freshwater primary productivity (Battin et al., 2009; Goodman et al., 2011). Both solutes are processed within aquatic ecosystems and are major contributors to aquatic food webs and primary productivity (i.e., metabolism) (Goodman et al., 2011; Wrona et al., 2016; Connolly et al., 2018).

To answer question 2a, I first explored the time series of flux (i.e., multiplying solute concentration by discharge) using a solute budget approach to identify periods of time when the lake is a net NO_3^- or DOC "sink" or "source". Generally, I expected that storm events would increase DOC and NO_3^- flux at both the inflow and outflow because storm events would alter lake residence time, nutrient uptake, and removal in Lake I8. As a result, I8 would have minimal removal effect on solute concentrations and may even become a source during storms. I also explored additional details of how DOC and NO_3^- concentration signals change as discharge increases at both the inflow and outflow monitoring stations by describing multiple concentration-discharge (C-Q) metrics during each storm event. Briefly, I estimated C-Q relationships by describing: 1) The linear relationship between log-log plots of C and Q and 2) The direction and magnitude of C-Q "hysteresis" and metrics. C-Q relationships provide insight into how carbon and nutrients behave and are mobilized during storm events to streams (Godsey et al., 2009; Minaudo et al., 2019). However, here with C-Q relationships at both the inlet and outlet of a lake, the C-Q metrics and hysteresis loops go beyond describing the traditional sourcing of solutes to streams, and they provide insight to both lake solute sourcing and the ability of the lake to modulate carbon and nutrient signals downstream of the lake. Further details

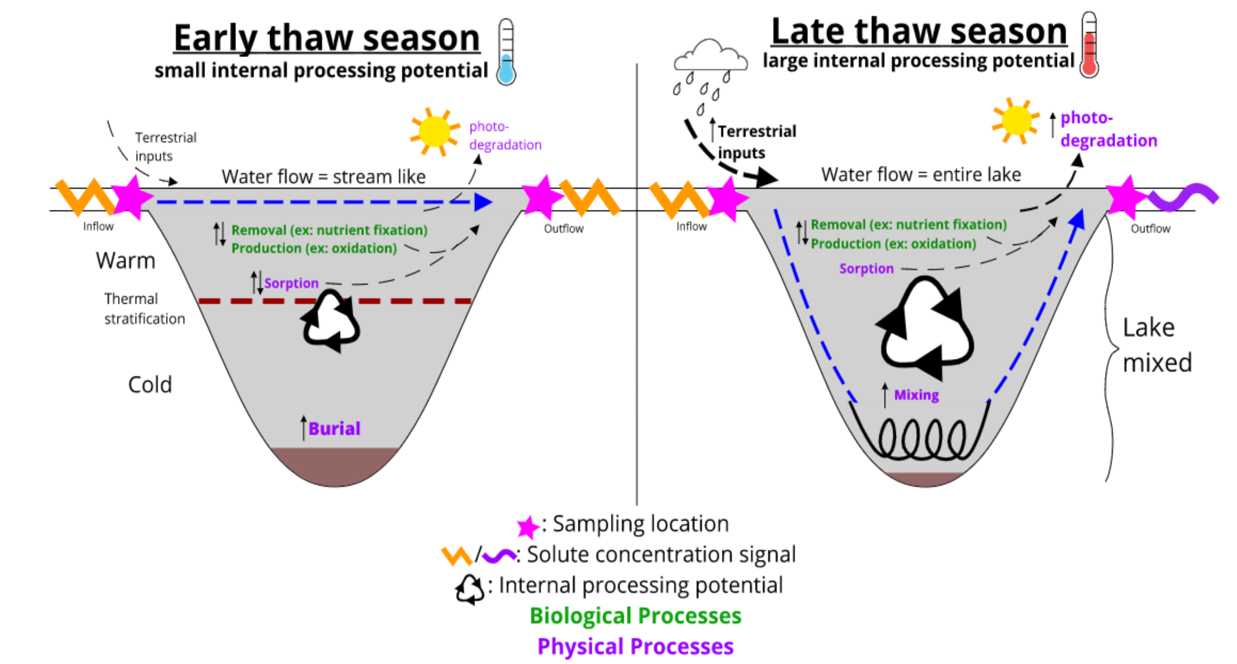

Figure 3.1.2: Conceptual model for the effect of seasonality and lake homogenization on lake internal processing potential and solute concentration signals. Green words are biological processes, and purple words are physical processes. The lake in the early thaw season will be thermally stratified, with low lake homogeneity and internal processing potential. Therefore, water will move rapidly through the lake in a stream-like fashion and limit the change in solute concentration signals. The lake in the late thaw season will have homogeneity and a higher internal processing potential. Terrestrial inputs will be greater, as will photo-degradation. Therefore, the solute concentration signal will have changed.

of C-Q metrics are described below in the Methods (Section 3.2.3). I compared C-Q metrics for individual storm pulses and metrics for two different seasons - early and late thaw season (Figure 3.1.2) to address Question 2b.

3.2. Materials and Methods

3.2.1. Site Description

Lake I8 is part of the largest tributary flowing into Toolik Lake known as the I-series watershed yet lies in a subcatchment apart from the main I-series lake chain sequence in a headwater stream and therefore has no upstream lake influence (Figure 3.1.1). Lake I8 is a small oligotrophic lake formed by glaciation ~10,000-12,000 years ago (Kling et al., 2000). The lake has a maximum depth of 8.5 m, surface area of 18.2 ha, and a total volume of 642,500 m^3. It drains a watershed area of 2,190 ha and has a total average residence time (RT) of 12.5 days (measured 2003-2007), ranging from a much longer average baseflow RT (284 days) to a shorter average stormflow RT (1.7 days) (Adams et al., 2014). Lake I8 has one main inflow and outflow stream both located on the deeper end (western side) of the lake where stream chemistry sensors were installed (Figure 3.2.1). While Lake I8 has additional inflow streams, these are typically ephemeral and only occasionally are activated during large storm events or spring snowmelt; together they contribute a relatively small amount of flow compared to the main inlet in most years (W. Bowden, *personal communications*). While water budgets have not been attempted recently, approximately 10 years ago, the Lake I8 main inflow stream accounted for ~80% of total lake inflow contribution over the entire thaw season (Adams et al., 2014). Lake I8 does stratify and is typically stratified until the end of July, when inflowing water and solutes only mix with the epilimnion. Later in the season (August), inflowing water mixes deeper in the lake hypolimnion as the inflowing stream water temperatures drop (Adams et al., 2014). This also results in water column mixing with the lake in the late summer season and early fall (i.e., end of the thaw season).

3.2.2. High-Frequency Water Quality Sensor Deployment at Lake I8

For Lake I8's inflow and outflow, I used high-frequency discharge data estimated from co-located, atmospherically compensated pressure transducers (Onset HOBO, Bourne

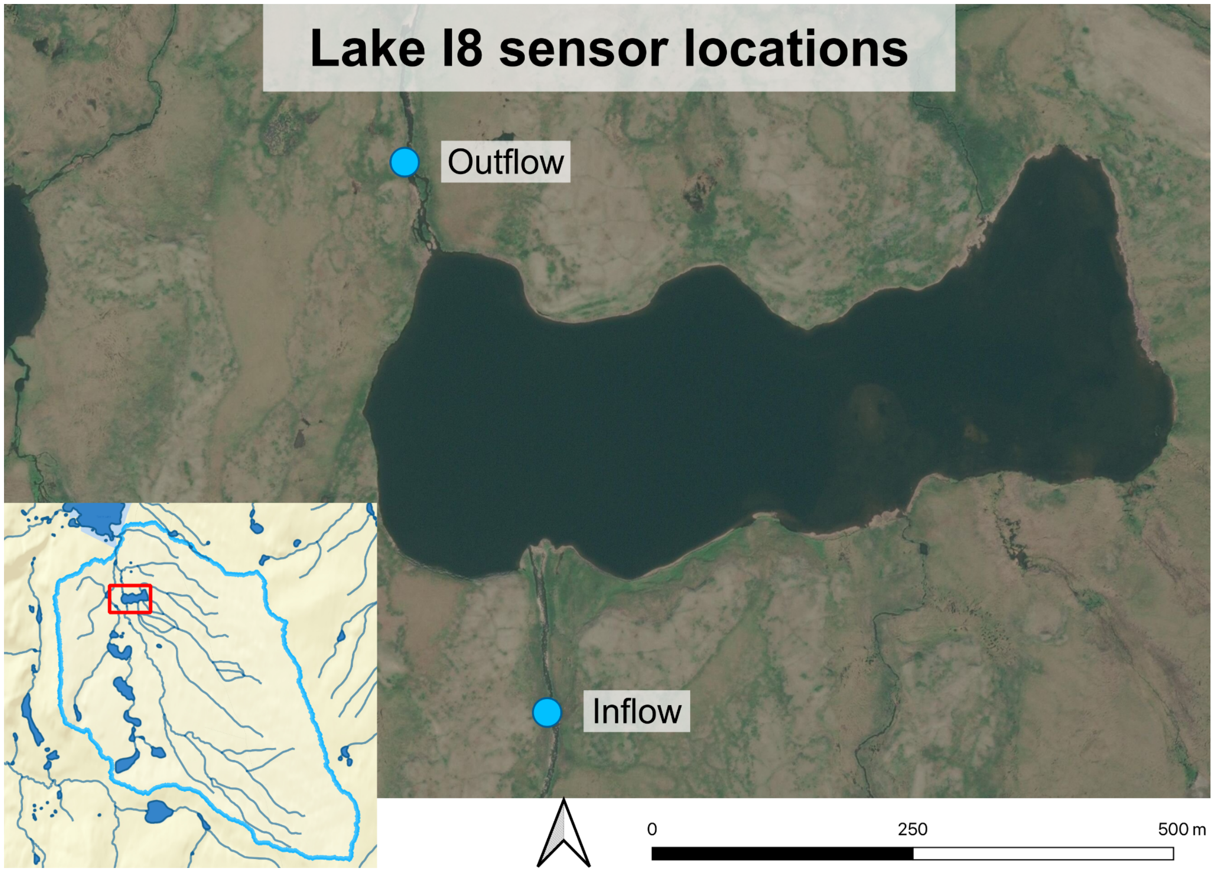

Figure 3.2.1: Satellite image of Lake I8 showing the inflow and outflow sensor installation locations, and the inset shows the lake location within the Arctic LTER I-series watershed.

Massachusetts, USA) that recorded water depth (i.e., stage) at 10-minute intervals. Stage data were then converted to discharge using a discharge-stage rating curve and velocity-area calculations generated from weekly field measurements during the thaw season (Perumal et al., 2007; Turnipseed and Sauer, 2010). Alongside discharge measurements, the dataset includes water chemistry collected at 15-minute intervals with in-situ, submersible UV-visible spectrophotometers (s::can Messtechnik GmbH, Vienna, Austria) installed at the inflow and outflow of Lake I8 during the majority of the 2019 thaw season (June 20–September 3). Each sensor was housed within PVC tubing and anchored above the streambed parallel to flow (Figure 3.2.2). These sensors optically measure nitrate (NO_3^-) and dissolved organic carbon (DOC). The spectrophotometers measure light absorbance at wavelengths from 220 through 750 nm

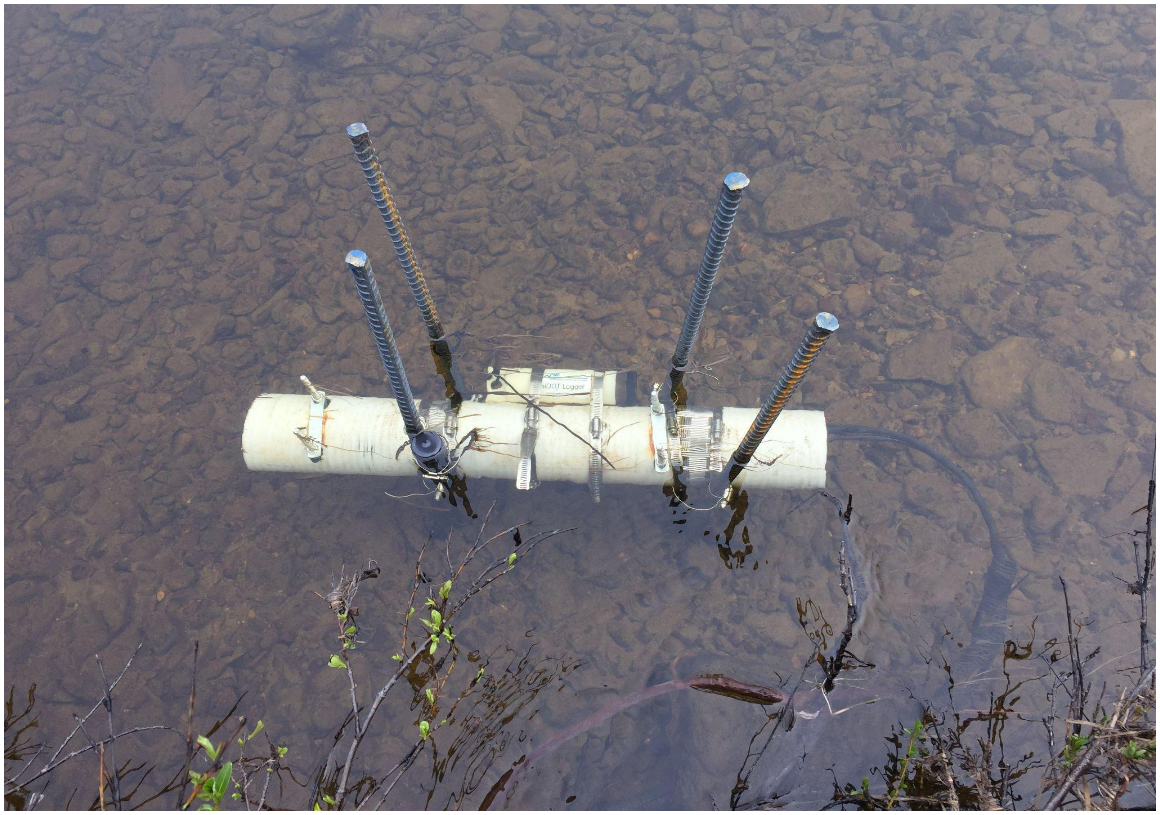

Figure 3.2.2: S::can in-situ UV-visible spectrophotometer encased in a PVC housing and anchored into the stream bed. Pressure transducer also housed and attached to the PVC.

(Edwards et al., 2001; Ruhala and Zarnetske, 2017) normalized for a 5 mm optical path length. The sensor data were calibrated, following Shogren et al. (2020), for DOC and NO_3^- concentration using a partial least squares regression (PLSR) model determined between the sensor spectra and concentration measured in samples taken biweekly throughout the summer. The sensor automatically cleans its lens with a rotating brush ~1 minute prior to collecting the absorbance reading, but the sensor lenses were also manually assessed and cleaned every 2 weeks during their deployment.

3.2.3. Concentration-Discharge Hysteresis and Metrics

To address how material sourcing may change during storms and throughout the thaw season, I quantified and described multiple relationships between observed concentration and discharge (C-Q) at Lake I8 inflow and outflow. I used both sets of high-frequency data to analyze flow regimes, storm event time frames, and solute concentrations. The timing and duration of storm events was determined using the discharge time series and the Lynne-Hollick (LH) baseflow filter implemented in R, which measures central tendency and baseflow indices (Lynne and Hollick, 1979). Baseflow is first calculated using the "baseflows" function in Hydrostats (Bond, 2019), with an α=0.99, for the entire time series. An average baseflow value is then calculated for the entire sampling period and used in the "high spell lengths" function in Hydrostats, which determines a start date and timing length (i.e., duration of storm event) for flows that increase 10% above the average baseflow value. Inflow baseflow was calculated and set at 0.47 m^3s^{-1}, and the outflow was set at 0.58 m^3s^{-1}.

With the storm events delineated, I then described the C-Q relationships that are expressed in each storm event using a series of established C-Q metrics that reveal process-based explanations of the observed C-Q dynamics. C-Q dynamics in streams during high flow events typically have hysteretic behavior, and this hysteresis occurs when there is a lag between pre- and post-storm solute concentrations relative to discharge. That is, concentration may vary following a cyclical relationship with storm discharge, typically forming either a clockwise or counterclockwise hysteretic loop (Evans and Davies, 1998). Hysteresis provides insight into a solute's source, storage, transportation, and processing (Rose et al., 2018; Lloyd et al., 2016). Various responses can occur during storm events depending on storm intensity, duration, and seasonality (Rose et al., 2018; Godsey et al., 2019; Minaudo et al., 2019), and to decipher these relationships, qualitative metrics are used. These metrics include the C-Q slope (β) of the log(C)-log(Q) linear regression, the ratio of concentration and discharge coefficient of variation

(CV_C/CV_Q), the hysteresis index (HI), and the flushing index (FI). The utility of these metrics is briefly described below.

A C-Q slope (β) indicates whether solutes flush or dilute at ranging intensities (slopes) during storm pulses (Burns et al., 2019). β ranges between +/- 1, where a $\beta > 0$ (positive slope) occurs when increasing solute flux (C) coincides with increasing water flux (Q) (i.e., solute flushing) and a $\beta < 0$ (negative slope) occurs when decreasing solute flux coincides with increasing water flux (i.e., solute dilution). When $\beta \approx 0$ (no slope) occurs, this indicates no or a weak directional relationship between concentration and discharge - also known as chemostasis (Godsey et al., 2009). To assist in describing C-Q relationships particularly when $\beta \approx 0$, calculating the ratio between concentration and discharge coefficient of variation (CV_C/CV_Q) analyzes the standard deviation of a variable normalized by its mean. More specifically, CV_C/CV_Q indicates whether variation in concentration is independent from discharge ($CV_C/CV_Q > 1$), or if discharge is the primary influence in concentration variability ($CV_C/CV_Q < 1$) (Rose et al., 2018).

The direction of the C-Q hysteresis also provides information about the location of solute sources from the terrestrial watershed relative to the stream channel. When the hysteresis curve travels clockwise, solute concentration increases rapidly during the onset of storm events, indicating solute mobilization proximal to the stream. Counterclockwise curves occur when solute concentration responds later in the storm event, indicating distal source contributions (Bowes et al., 2009). A hysteresis index (HI) relates to the magnitude and direction of the hysteresis curve. HI ranges from +/-1 where positive values are clockwise curves (proximal sourcing), and negative values are counterclockwise (distal sourcing). Additionally, the larger the HI value (i.e., closer to +1 or -1), the larger the difference between concentrations of the rising and falling limb at similar discharge values. Finally, to provide insight into initial storm concentration response, flushing index (FI) analyzes directional concentration change from the storm onset to peakflow. FI ranges between +/- 1, where a FI>0 (positive slope) indicates solute flushing during the storm rising limb and a FI<0 (negative slope) indicates solute dilution during storm rising limb.

Lastly, biplots of the various above C-Q metrics are used to compare solute transport conditions at the inflow and outflow of Lake I8. They provide further insight into solute sourcing, routing, and processing patterns throughout the thaw season above and below the lake. For instance, inflow versus outflow β compared to FI shows solute directionality of the entire storm event compared to just the rising limb, inflow versus outflow β to HI indicates storm event solute directionality and solute source distance from stream, and inflow versus outflow HI to FI indicates solute source distance from stream and rising limb directionality. Ellipses were used to draw a circular 95% confidence interval around multivariate normal distribution data. Ellipses show a visual summary of data scatter within biplots and help visualize the relationship between inflow and outflow C-Q direction and behavior (Shogren et al., 2020b). For example, data that are more scattered and variable will have larger/wider ellipses, whereas data that are generally less variable will have smaller ellipses.

3.3. Results

3.3.1. Biogeochemical Modulation of an Arctic Lake During Storm Events

High-frequency discharge (Q), DOC, and NO_3^- at the inflow and outflow of Lake I8 demonstrate that flow and solute concentrations were highly variable during the study period (Figure 3.3.1). In total, five storm events were captured throughout the thaw season, two in the

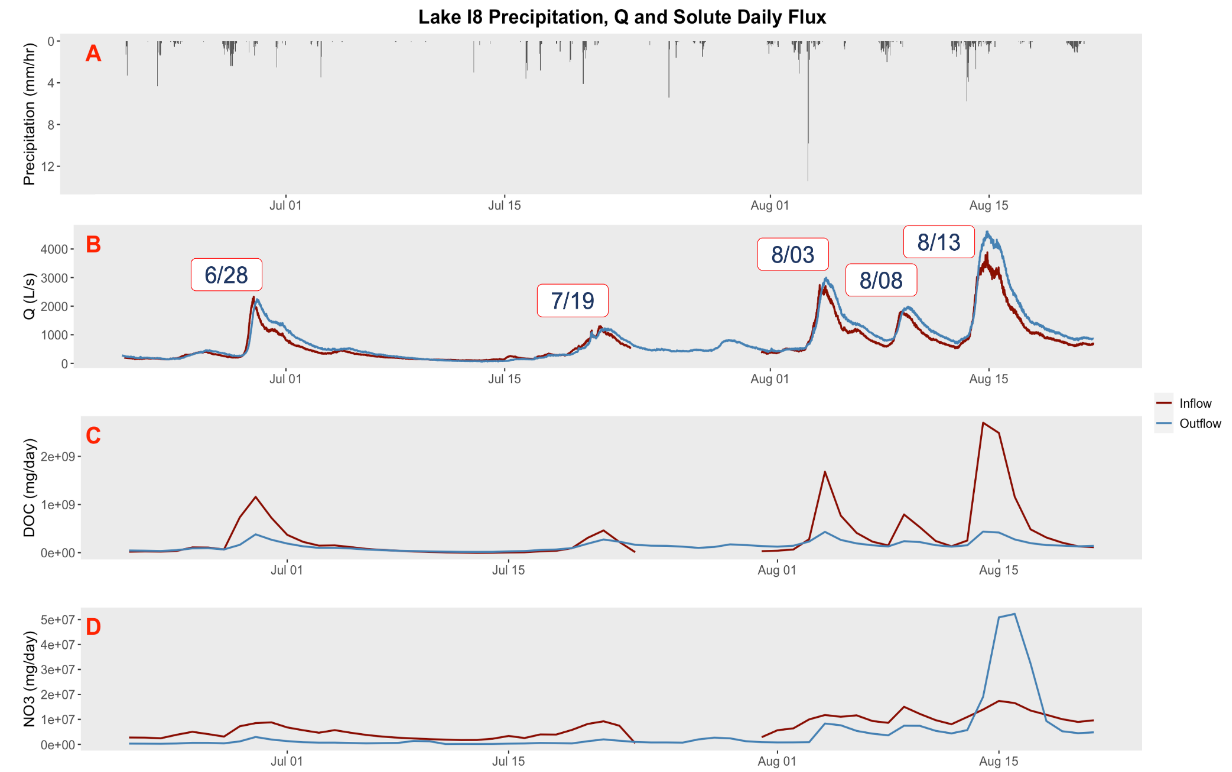

Figure 3.3.1: Time series plot of *(A)* hourly precipitation, *(B)* high-frequency discharge (Q), *(C)* daily flux of DOC, and *(D)* daily flux of NO_3^- at Lake I8 inflow (red) and outflow (blue) throughout the 2019 thaw season. Precipitation data collected at Toolik Field Station Weather Station (Environmental Data Center Team, 2021). Solute concentrations were converted to daily flux for a smoother visual line. Storm event start dates are labelled within the corresponding Q panel.

early season (June-July) and three in the late season (August-September), which were then delineated to determine timing and duration. Storm event dates were applied to all measured nutrients. While there is a general increase (flushing) of solute concentrations at both the inflow and outflow of Lake I8 during storm event flows, the concentrations dynamics of DOC and NO_3^- are distinct between the inflow and outflow, whereas the difference in Q is less distinct between inflow and outflow (Figure 3.3.1).

Concentrations of DOC and NO_3^- are compared to Q during the storm events to provide insight into the lake effects on downstream C-Q conditions. The inflow C-Q trends for both DOC and NO_3^- follow a more linear trajectory (i.e., minimal hysteresis), concentrations

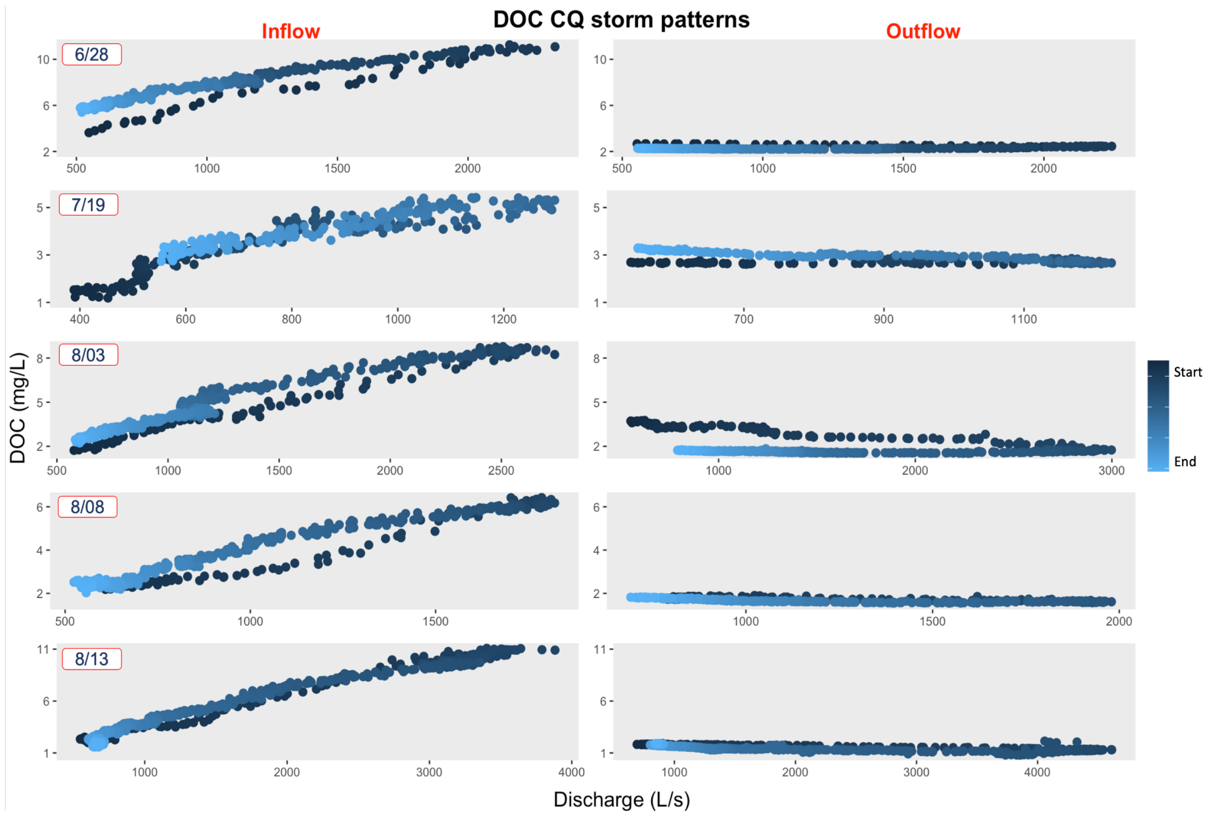

Figure 3.3.2: DOC C-Q storm patterns at Lake I8's inflow (left panel) and outflow (right panel) during the five monitored storm events. Storm event start dates are labelled in corresponding rows. Storm onset is indicated with dark blue points and progressively brightens to the end of the storm with light blue points.

increase/decrease along the same line during the rising and falling limb of a storm, whereas the outflow C-Q trend is more complex and variable yet dilute compared to the inflow (Figure 3.3.2 & Figure 3.3.3). During these storm events, Lake I8 significantly buffers both DOC and NO_3^- dynamics and acts as an overall solute sink. The only storm event that had higher solute concentrations at the outflow was for NO_3^- during the last storm event of the sampling period (August 13th; Figure 3.3.3). This storm event also had the highest discharge and overall concentration flush of all observed storms. Still, the overall C-Q pattern of this storm is similar to the others, except for a larger increase in NO_3^- concentrations.

By describing C-Q metrics at the annual scale (i.e., across the entire season), I characterized the general availability and mobilization patterns of NO_3^- and DOC in Lake I8

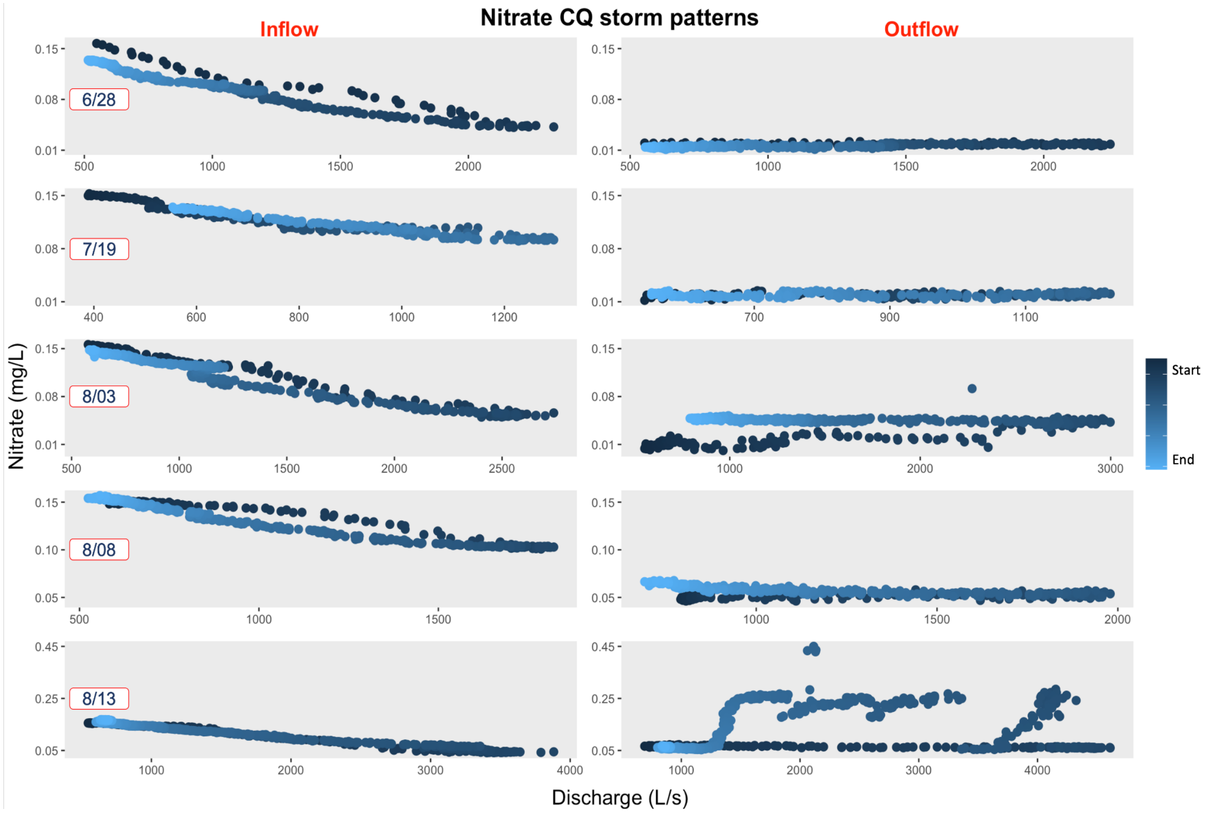

Figure 3.3.3: NO_3^- C-Q storm patterns at Lake I8's inflow (left panel) and outflow (right panel) during the five monitored storm events. Storm event start dates are labelled in corresponding rows. Storm onset is indicated with dark blue points and progressively brightens to the end of the storm with light blue points.

inflow and outflow stations. The C-Q metrics slope (β), flushing index (FI), hysteresis index (HI), and the ratio of coefficient of variation (CV) for concentration to discharge (CVc/CVq) further quantitatively illustrate the influence I8 has on NO_3^- and DOC export from the I8 subcatchment (Figure 3.3.4). The C-Q β during storm events for NO_3^- at the inflow was consistently indicative of diluting, whereas β for DOC at the inflow was consistently flushing. This consistent inflow behavior for both solutes is not observed at the outflow; NO_3^- consistently flushes and DOC dilutes at the outflow. The inflow slope values are on the extreme ends (near +/-1) of flushing and diluting yet are buffered (~0) at the outflow (Figure 3.3.4.A). ANOVA tests confirm both NO_3^- and DOC β are significantly different based on inflow and outflow with lake influence (p-value<0.0005). Flushing Index had similar results to β, where NO_3^- dilutes at the

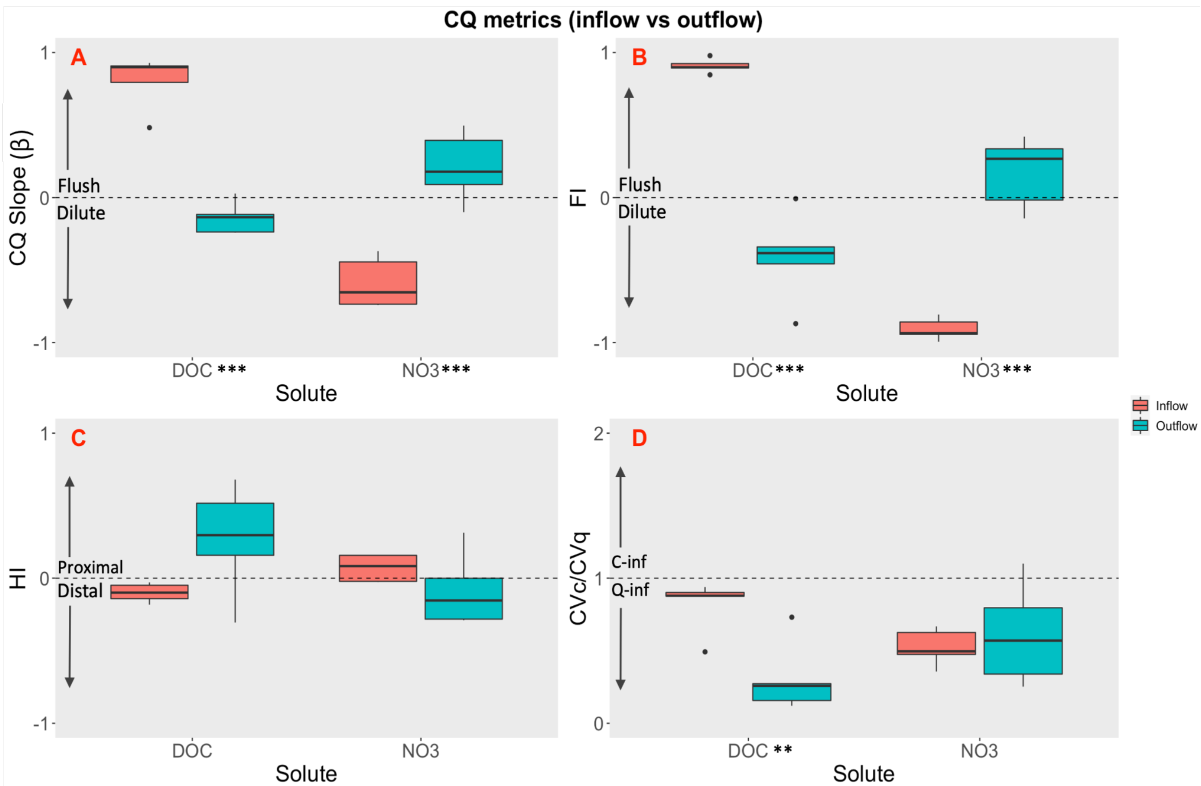

Figure 3.3.4: Boxplots of DOC and NO_3^- C-Q metrics for Lake I8's inflow (salmon) and outflow (turquoise) over an entire thaw season. Dashed black lines delineate differences in solute transport dynamics (panel A, B, and D) or source proximity (panel C). Each panel is annotated with the difference in transport or source. Boxplots indicate the median concentration value with the solid black horizontal line and the lower and upper hinges (the 25th and 75th percentiles) are shown with colored boxes. Whiskers extend to 1.5*IQR (interquartile range), and any points beyond are outliers. Asterisks are present next to the solute with significant difference between inflow and outflow C-Q metrics based on ANOVA tests (p-value<0.05 [*], p-value<0.01 [**], p-value<0.001 [***]).

inflow but flushes at the outflow, and DOC flushes at the inflow but dilutes at the outflow. Within individual storm events, lake buffering occurs during storm rising limbs as well, as both NO_3^- and DOC outflow is nearer to 0 (Figure 3.3.4.B). Additionally, ANOVA test results for NO_3^- and DOC FI indicate high significance in their difference (p-value<0.0005). Hysteresis Index indicates inflow NO_3^- during storm events was more proximal to the stream (HI>0), whereas outflow NO_3^- was more distal to the stream (HI<0). DOC HI at the inflow indicated that the DOC source was more distal but switched at the outflow to a more proximal source (Figure

3.3.4.C), although, ANOVA tests suggest that neither NO_3^- nor DOC HIs were significantly different (p-value >0.06). The CV_C/CV_Q values indicated that both solute concentrations were largely influenced by variations in discharge (Figure 3.3.4.D). Specifically, Q was still mostly influential for both NO_3^- and DOC at the inflow and outflow, DOC at the inflow was less influenced by Q than at the outflow (p-value <0.001).

Biplots of C-Q metrics provide a comparison of inflow and outflow direction and behavior during storm events (Figure 3.3.5). The biplots show inflow conditions are usually tightly grouped into one quadrant indicative of consistent C-Q behavior through the storms and season, whereas outflow conditions are more scattered, indicative of more complex and variable C-Q behavior across storms and season. For example, inflow showed consistent β, HI, and FI

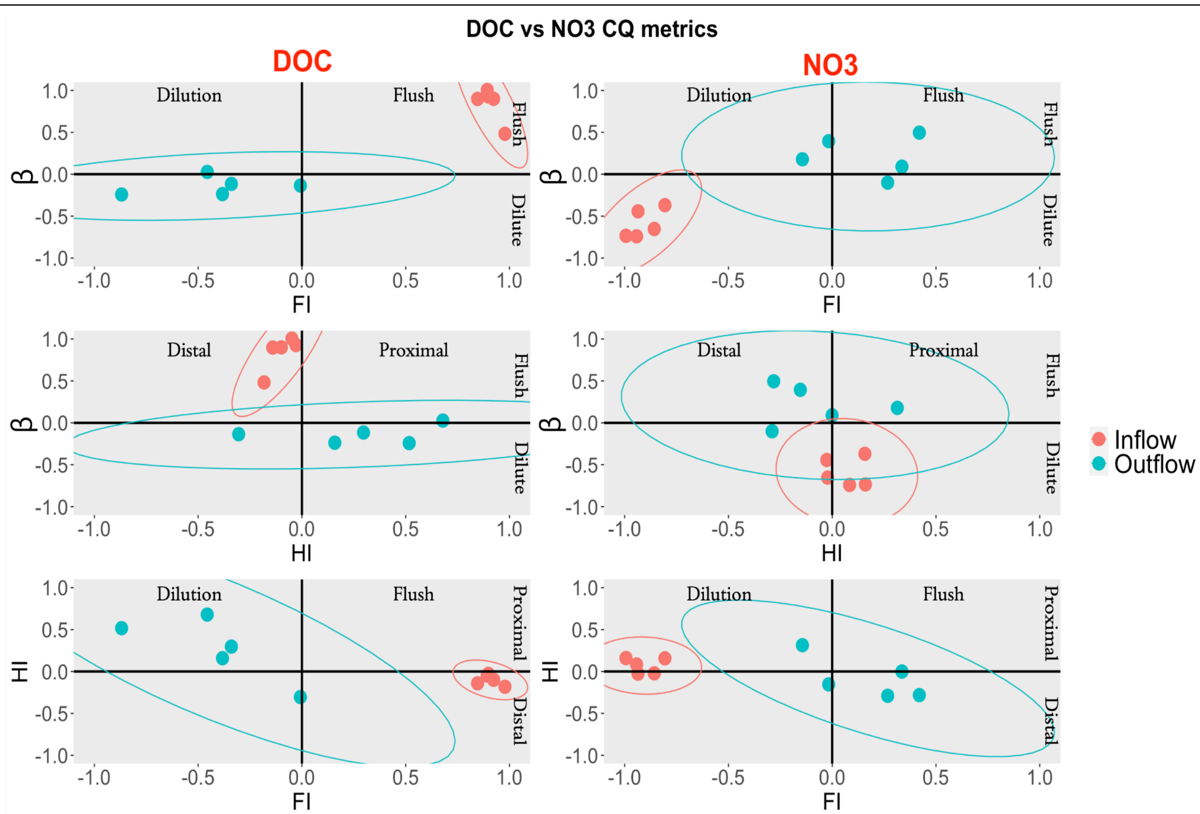

Figure 3.3.5: Biplots of DOC and NO_3^- β vs. FI, β vs. HI, and HI vs. FI for Lake I8 inflow (salmon) and outflow (turquoise). Each quadrant represents a combination of two C-Q behaviors, which are annotated within each biplot. Solid black horizontal and vertical lines indicate behavior that is chemostatic (β and FI = 0) or non-hysteretic (HI = 0). Ellipses represent the 95% confidence level around the inflow and outflow C-Q points.

values indicative of rapid DOC flushing from less-connected and more distal sources to the inflow stream, whereas DOC at the outflow showed more dilution behavior and at times coming from connected or in-lake sources. NO_3^- at the inflow showed β, HI, and FI values indicative of dilution from proximal sources, whereas NO_3^- at the outflow showed a wide scatter between flushing and diluting mostly from distal sources.

To establish a baseline relationship between C-Q β and CV_C/CV_Q within Lake I8, I calculated C-Q metrics at inter-storm (between storm) time periods and then compared them to the intra-storm (during storm) C-Q metrics (Figure 3.3.6). Based on ANOVA tests, inflow NO_3^- β (p-value =0.012) and CV_C/CV_Q (p-value = 0.003) were significantly different between inter- and intra-storm periods, as well as inflow DOC CV_C/CV_Q (p-value = 0.02). None of the outflow

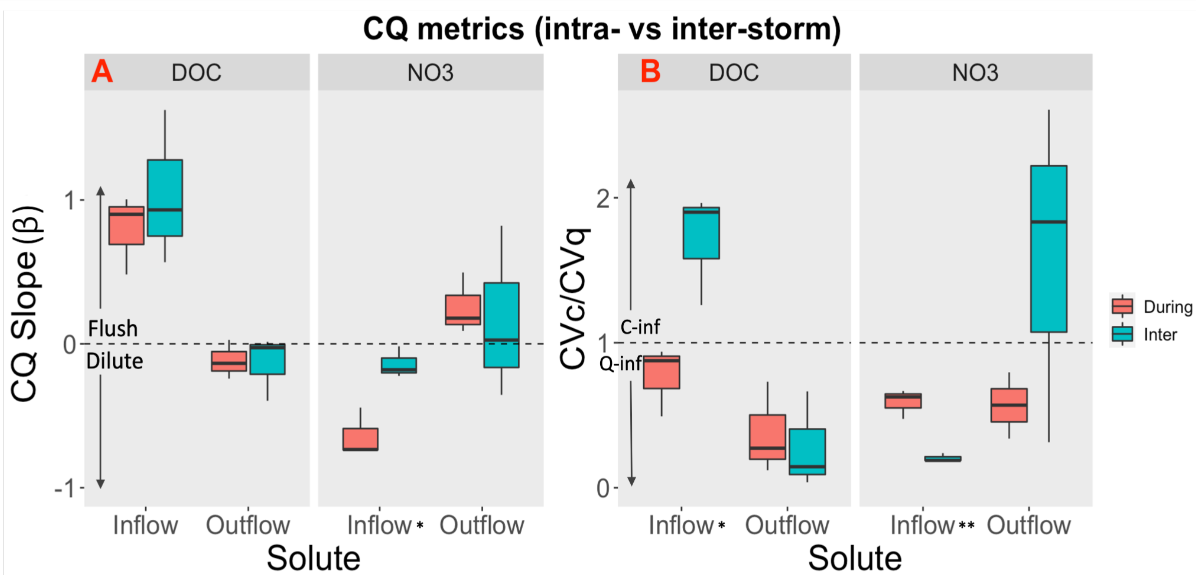

Figure 3.3.6: Boxplots of DOC and NO_3^- C-Q metrics for Lake I8's intra-storm (salmon) and inter-storm (turquoise) over an entire thaw season. Dashed black lines delineate differences in solute transport dynamics (panel A and B). Each panel is annotated with the difference in transport dynamics. Boxplots indicate the median concentration value with the solid black horizontal line and the lower and upper hinges (the 25th and 75th percentiles) are shown with colored boxes. Whiskers extend to 1.5*IQR (interquartile range), and any points beyond are outliers. Asterisks are present next to the solute with significant difference between intra- and inter-storm C-Q metrics based on ANOVA tests (p-value<0.05 [*], p-value<0.01 [**], p-value<0.001 [***]).

metrics nor DOC inflow β were significantly different (p-value >0.2) when comparing inter-storm to intra-storm.

3.3.2. Lake Biogeochemical Modulation During Early vs Late Thaw Season Storm Events

To gain further insight into the C-Q conditions at the inflow and outflow, I assessed the historical vertical temperature profile records for stratification condition from 2010-2017 in Lake I8 via the Environmental Data Initiative as part of the Arctic LTER (Giblin and Kling, 2019). These temperature profiles are only typically collected three times during a thaw season. Still, they demonstrate that water temperature and stratification conditions change throughout the thaw season in Lake I8 (Figure 3.3.7). In the early thaw season (June), Lake I8 is most often stratified with surface waters being warmer with a distinct shift to colder water at depth. As the thaw

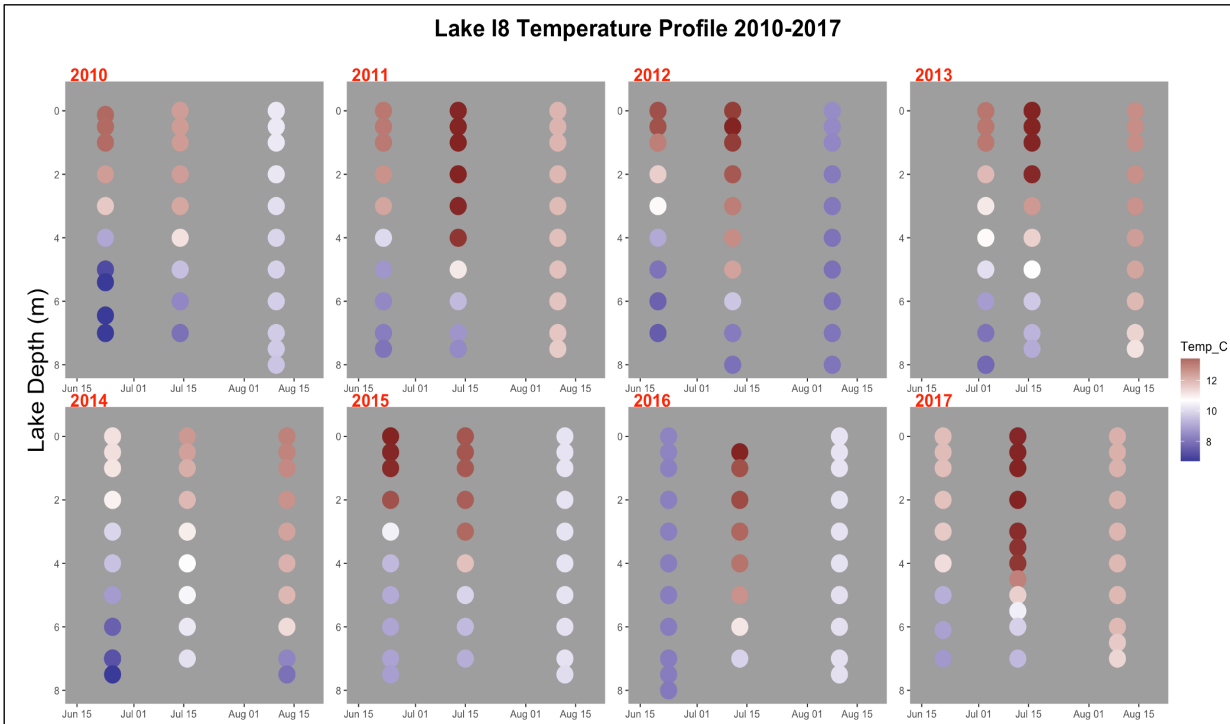

Figure 3.3.7: Lake I8 temperature profiles for three days (between June and August) throughout the thaw seasons of 2010-2017. Temperature is plotted with regard to lake depth, where shallow depths are represented at the top of each panel, and deeper in the water column is lower on the y-axis. Data retrieved from the Environmental Data Initiative (Giblin and Kling, 2019).

season progresses into July and August, the water temperatures begin to homogenize with less stratification and warmer waters at depth. There was no Lake I8 temperature profile data available during the C-Q data collection in 2019, however, the general seasonal temperature profiles and stratification were consistent in each of the eight prior years.

Despite changing lake thermal regimes, a comparison of the early storm events (June-July) to late storm events (August-September) showed minimal change in nutrient C-Q metrics at the inflow or outflow (Figure 3.3.8). Based on ANOVA tests, no significant differences were

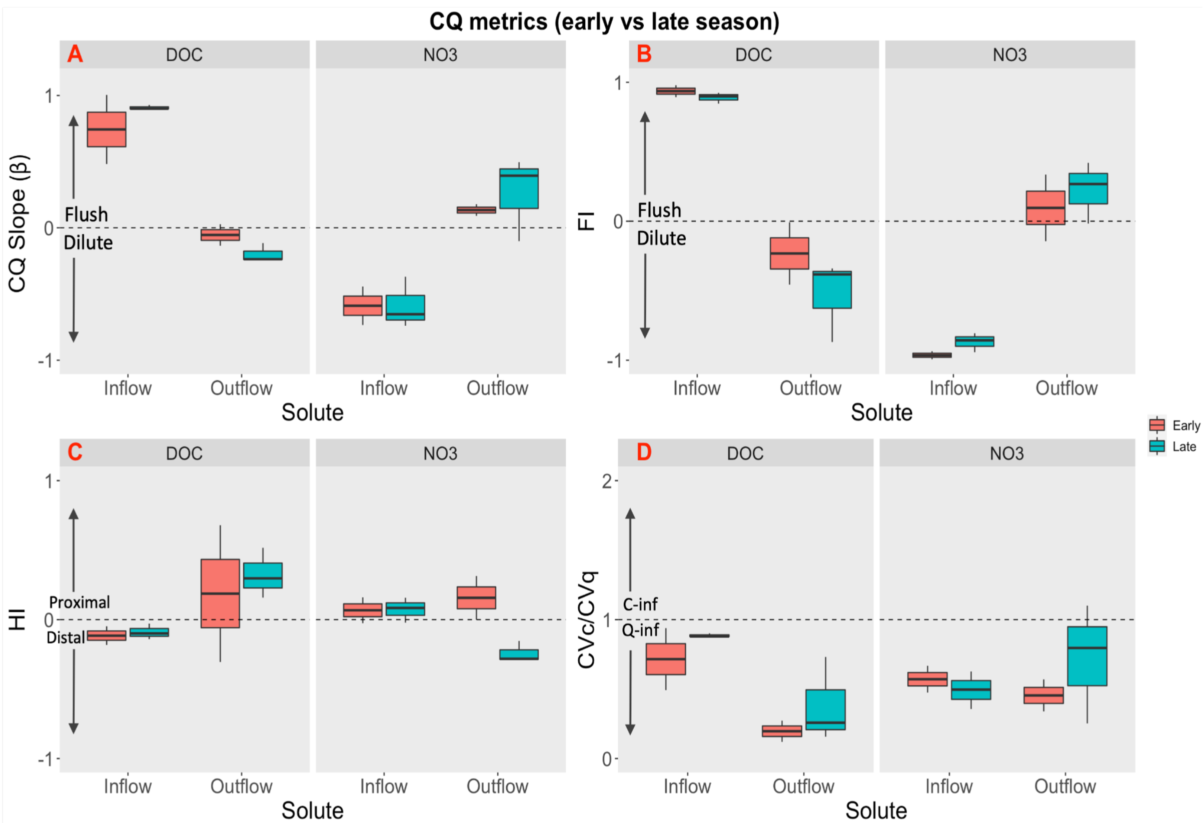

Figure 3.3.8: Boxplots of DOC and NO_3^- C-Q metrics for storm events in the early season (salmon) and late season (turquoise). Dashed black lines delineate differences in solute transport dynamics (panel A, B, and D) or source proximity (panel C). Each panel is annotated with the difference in transport or source. Boxplots indicate the median concentration value with the solid black horizontal line and the lower and upper hinges (the 25th and 75th percentiles) are shown with colored boxes. Whiskers extend to 1.5*IQR (interquartile range), and any points beyond are outliers. Asterisks are present next to the solute with significant difference between early and late season C-Q metrics based on ANOVA tests (p-value<0.05 [*], p-value<0.01 [**], p-value<0.001 [***]).

calculated between early and late storms at the inflow or outflow for NO_3^- or DOC (p-value >0.05). Only one minimal significance was found for NO_3^- HI at the lake outflow (p-value = 0.055). Hence, C-Q metrics were mostly significantly different by whether they were at the inflow or outflow and not by the seasonality during the thaw season.

3.4. Discussion and Conclusion

Using high-frequency data and C-Q relationships in Lake I8 provided a detailed and insightful look into how the lake modulates biogeochemical signals between the inflow and outflow during storm events. The C-Q analysis showed evidence that Arctic lakes likely change solute transportation and sourcing during storm events, as seen in DOC and NO_3^- in Lake I8 that consistently showed a buffering of concentration variability at the outlet, reduction of DOC, and increase of NO_3^-. To further understand how stream-lake interactions modulate biogeochemical signals in the Arctic, continued high-frequency data collection and an expansion of studied stream-lake interaction locations is necessary to determine if the findings from Lake I8 are consistent across years and are representative of other Arctic lakes.

3.4.1. C-Q Relationships Throughout a Thaw Season in an Arctic Lake

Precipitation events during the thaw season typically resulted in similar increased discharge events at both the inflow and outflow of Lake I8, but the observed solute responses were very different between inflow and outflow. The nearly identical discharge dynamics at the inflow and outflow indicate similar hydrologic routing of water above and below the lake with only a small lag created by the travel time through the lake. Whereas the biogeochemical signals and concentrations for DOC and NO_3^- were highly modified between the inflow and outflow. Still, the net result on biogeochemical fluxes during storm events is that DOC and NO_3^- flux through the watershed increases showing storm events flush nutrients to aquatic systems and that Lake I8 biogeochemical modulation capacity is more dependent on Q variability, as other studies have seen (Stieglitz et al., 2003; Adams et al., 2015). So, while the lake can modulate biogeochemical conditions observed downstream, discharge variability during storms is likely the dominant control on watershed flux in the Lake I8 subcatchment. This is consistent with large-scale, multi-biome assessments that show the dominance of hydrologic transport-limitation during storm events in river networks (e.g., Raymond and Saiers, 2010; Zarnetske et al., 2018)

C-Q patterns and calculated C-Q metrics during the storms enhance our understanding of the mobilization and transformation of biogeochemical signals (Godsey et al., 2009; Minaudo et al., 2019). Here, they indicate that the Lake I8 does have some important modulation effects on DOC and NO_3^- transport out of the subcatchment. Lake I8 buffers the measured inflowing solutes (i.e., reduces magnitude of variability and changes total mass transport) as concentration diluted at the lake outflow during storm events, as well as near-zero β values during these same storm events. β values also indicated a switch between inflow and outflow processing, where inflow DOC β was flushing then diluting at the outflow. NO_3^- β also switched from diluting at the inflow to flushing at the outflow. In other words, Lake I8 is a DOC sink and NO_3^- source during storm events. Comparatively, in nearby Arctic LTER watershed scale studies with high stream-lake interaction presence, DOC showed increased solute concentrations during storm events, while NO_3^- was typically source-limited at the outlet of the large watershed that contained dozens of lakes and a drainage area an order of magnitude larger than that of Lake I8 (Shogren et al., 2020b). That watershed scale pattern of DOC and NO_3^- C-Q behavior diverges from this detailed analysis of Lake I8 C-Q behavior. So, there is likely a scale dependence, and the spatial arrangement of stream-lake interactions controls what is seen at one lake versus what is seen at the watershed scale. Still, the present study, when compared to the watershed scale study, highlights that there is still more work needed to understand the biogeochemical modulation role of stream-lake interactions within a larger watershed context (Goodman et al., 2011).

The C-Q biplots emphasize the overall solute relationship and behavioral differences during storm events between the inflow and outflow of Lake I8 (Shogren et al., 2020b). Typically, inflow DOC remained in one quadrant indicating flushing from a distal source throughout thaw season storm events which is consistent with often observed transport-limitation behavior of DOC in stream networks (Zarnetske et al., 2018). This transport-limitation signal is largely altered at the outflow when DOC is more dilute and proximal. At the outlet, C-Q variance is also larger, and the confidence level ellipses spread across all four quadrants indicating that the lake is introducing more complexity and interacting processes that control C-Q behavior. Additionally, NO_3^- showed inverse results to the DOC as it generally enriched at the lake outlet, but unlike DOC it had similar inflow and outflow variability. The NO_3^- inflow was typically diluting and had evidence of proximal sourcing, and the outflow was scattered between dilute and flushing and derived from mainly distal sourcing.

The comparison between intra-storm to inter-storm C-Q metrics showed that C-Q modulation below the lake was present throughout the thaw season, but that storm events alter both inflow and outflow of DOC and NO_3^-. First, significant differences in NO_3^- β (p-value > 0.05) were calculated at the inflow site between intra- and inter-storm events (Figure 3.3.6). Inter-storm time periods showed a buffering for NO_3^- ($\beta \approx 0$), but significantly diluted (p-value < 0.05) during storm events. Meanwhile, inflowing DOC remained consistently flushing during intra and inter-storm events. However, after lake influence, the biogeochemical signals for DOC and NO_3^- showed no significant differences between intra- and inter-storm events (p-value > 0.05). Previous studies have also found that lakes can act as "buffers" for solute signals in temperate-zone watersheds (Goodman et al., 2011; Baker et al., 2016), but this study is the first to demonstrate it for an Arctic lake with such high-temporal resolution. Additionally, while not directly studied with high-frequency measurements, there was evidence in one Arctic watershed study that lakes generally buffer variability in upstream biogeochemical concentrations (Shogren et al., 2019). While the results from that study and previous studies point to lakes as biogeochemical buffers based on low-frequency measurements across multiple lakes, the present study showcases novel high-frequency results that demonstrate DOC and NO_3^- conditions switch from flushing and diluting between the inflow and outflow of a lake, providing insights into lake nutrient processing. It is clear that C-Q metrics and relationships provide a unique and detailed look into how biogeochemical signals are processed within Lake I8. Future investigations, such as detailed lake metabolism, isotopic C/N tracer, and hydrodynamic studies, are necessary to go beyond the lake "black box" approach of this study and characterize the internal lake conditions and biogeochemical processes that are interacting with lake DOC and NO_3^-.

3.4.2. Lake Mixing and C-Q Metrics Between Early and Late Thaw Season

Arctic streams and lakes have a dynamic physical and solute processing potential. Lakes are typically stratified in late spring to early summer and are subjected to unique nutrient processing, temperature, and light variations (MacIntyre et al., 2006). In late spring, runoff is dominated by snowmelt, yet rapid warming occurs in stream waters and lake upper water column layers even with ice cover, causing the distinct thermocline (Kling, 2009; Cortés and MacIntyre, 2019). This plays an important role in the hydraulic routing of water and solutes into and through a lake as the lake thermocline would inhibit mixing through the water column between the inflow and outflow. In late summer at Lake I8, stream temperatures begin to drop, permeating through the lake thermocline (Heim et al., 2016; King et al., 2016). This causes a drop in lake temperature that induces vertical mixing, as shown in Figure 3.3.7, increasing the residence time and enhancing the capability for nutrient processing in the lake (MacIntyre et al., 2006). This increased mixing was expected to result in different DOC and NO_3^- modulation in the lake, via processes like NO_3^- uptake, or DOC production, but there was no apparent difference in nutrient processing for the majority of C-Q metrics between early and late season storms despite likely very different lake stratification and mixing conditions. DOC lacked any difference between early and late thaw season storm events indicating a consistent release and processing of DOC from the terrestrial parts of the watershed and within the lake. Results from DOC early versus late storm events concur with previous studies finding DOC was consistently flushed throughout thaw season storm events (Petrone et al., 2006). The size of the storm event flow may be a factor in overwhelming any effect of seasonal stratification and mixing in the lake as the lake is relatively small and has an estimated storm flow residence time of only 1.7 days, which means there is minimal time for internal lake processing of solutes during storms.

Notably, the storm event on August 13th had a unique effect on outflow NO_3^- compared to all previous storm events, as shown through NO_3^- daily flux and NO_3^- outflow C-Q storm pattern (Figure 3.3.1.D & Figure 3.3.3.E). While daily flux appears to have substantially flushed NO_3^- from the lake, this did not greatly affect β or FI. NO_3^- typically flushed at the outflow during the entire thaw season, yet the considerable increase in daily flux for the August 13th storm could be largely due to decreased autotrophic demand for NO_3^- that can happen during wet periods in this region (Harms and Jones, 2012). Additionally, as thaw depth increases in the surrounding landscape, flow paths deepen allowing increased NO_3^- flushing from deeper soils that have higher inorganic nitrogen reserves and nitrogen remineralization rates (Nadelhoffer et al., 1991; Khosh et al., 2017). Results from early versus late season storm event HI may confirm findings from these previous soil NO_3^- studies since early season NO_3^- HI alluded to more proximal solute sourcing (i.e., within or near-stream), whereas late season NO_3^- HI was more distally sourced (i.e., hillslope). Despite the change in NO_3^- sourcing between early and late season, no other changes were seen in processing or dynamics. When taken together, the influence of landscape-scale deeper hydrologic flow paths and decreased microbial activity seem to dominate over lake controls on NO_3^- during storm events in the Lake I8 subcatchment.

3.4.3. Study Limitations and Future Directions

A few areas of concern come from the lack of multi-year observations of Lake I8 inflow and outflow conditions. Only two storms were monitored in the early season, and three in the late thaw season. Hence, it is not known if these observations are representative of other years in Lake I8 and we have limited storm observations to assess overall C-Q behavior and even less confidence in subsampling them as early and late thaw season. There was also a large break in data when the inflow sensor malfunctioned, and an additional storm was missed. An additional year, spanning more of the thaw season, was planned as a part of this study, but was not possible due to lack of access to Arctic field sites during the COVID-19 pandemic. In the 2021 thaw season, a similar sampling design was deployed at the inflow and outflow of Lake I8, and future projects will be able to reassess the C-Q conditions observed in the 2019 data of this study. Calculating the C-Q metrics of more thaw season storms would help to confirm or refute the above interpretations about how lakes process storm event solute pulses.

Using high-frequency sensors to collect further detailed information about hydrological and ecological conditions of stream-lake interactions helps identify specific processes controlling individual solutes in Arctic lakes. In this study, I treated Lake I8 as a “black box”, speculating about possible lake and watershed nutrient processing controls on DOC and NO_3^-. To further examine storm events and seasonal lake processing, logging high-frequency data within the lake at different depths (i.e., above and below the thermocline) could reveal a more enhanced understanding of nutrient controlling processes (e.g., lake metabolism, specific microbial mineralization pathways, and geogenic controls like Fe-DOC interactions). Further, a mass balance approach of closing the C or N budget of the lake would further help assess physical versus biogeochemical controls on the stream-lake interaction effect on DOC and NO_3^- at the Lake I8 subcatchment scale. Any additional observations, experiments, or modeling of internal lake processes will advance us past the simple “black box” approach used for Lake I8 in this study.

3.4.4. Conclusion and Broader Implications

This study presents high-frequency data to assess C-Q conditions for DOC and NO_3^- at the inflow and outflow of an Arctic lake. It provides insights into how stream-lake interactions in the Arctic can modulate watershed DOC and NO_3^- conditions in a stream network. Furthermore, this study reveals both how water flowing into and out of a lake behaves during storm events, which is relevant not only to understanding stream-lake interaction effects on biogeochemistry, but also because much of the Arctic is predicted to become more hydrologically dynamic with more frequent and larger storms (Solomon et al., 2007; Rawlins et al., 2010; Bring et al., 2016). Understanding the role of lakes in biogeochemical research of the Arctic as well as hydrologic variability are critical missing pieces to understanding and predicting future biogeochemical and ecological conditions of the Arctic.

In other studies, storm events have been shown to increase nutrient flux into aquatic ecosystems (Raymond and Saiers, 2010) and this study showed that is also the case in the Lake I8 watershed. Temperate region stream-lake interactions have shown lakes modulate biogeochemical signals through a comparison of C-Q metrics during storm events and seasonal variation (Rose et al., 2018; Minaudo et al., 2019). This study showed Arctic stream-lake interactions also modulate biogeochemical signals during storm events, with strong buffering of inflow variability at the outlet for DOC and NO_3^-, and overall DOC removal and NO_3^- increases as water moves into and out of Lake I8.

Further collection of high-frequency, high-resolution data has already advanced hydrologic and biogeochemical studies around the world, and continued collection of high-frequency data in understudied parts of the world, like the Arctic, is necessary for improved models of steam-lake interactions, rivers, and the climate (Burns et al., 2019). This study showed stream-lake interactions modulate solutes within a single lake system, but other studies have analyzed the effects of stream-lake interactions within a larger watershed context (Shogren et al., 2020b). Further study of how multiple stream-lake interactions may modify watershed-scale DOC and NO_3^- conditions is needed. Being able to distinguish lake biogeochemical effects within a river network is necessary for improving Arctic environmental change models (McGuire et al., 2018) and evidence-based management planning and practices needed in changing landscapes like the rapidly warming and changing Arctic (Lique et al., 2016; Burns et al., 2019; Heino et al., 2020).

CHAPTER 4: SYNTHESIS

This thesis focused on the role of stream-lake interactions on changing biogeochemical signals within Arctic river networks. Previous studies have found lakes change biogeochemical signals (i.e., the amount and timing of solutes moving through and out of watersheds) (Goodman et al., 2011; Baker et al., 2016; Shogren et al., 2019). Yet, stream-lake interactions are understudied parts of watersheds, especially in remote and rapidly changing environments such as the Arctic. This study was conducted in two main studies, with two guiding questions per study. The guiding research questions for the first study (Chapter 2) were based mostly on how biogeochemistry varies in space as a function of stream lake interactions: A) How do biogeochemical signals compare between subcatchments with increasing lake abundance; and B) How does the amount of time water (and solutes) spend in a lake influence the biogeochemical signals leaving the lake and ultimately what flows out of the watershed containing the lake? To address these questions, a spatially extensive study was conducted throughout Oksrukuyik Creek watershed on the North Slope of Alaska. Synoptic samples (i.e., water grab samples) were repeatedly collected at 29 sampling locations in June and August of 2016, 2017, and 2018. Each sample was analyzed for a suite of biogeochemical solute concentrations. Additionally, stream instantaneous discharge was measured at many sites across the watershed to help estimate the amount of water flowing into and out of Oksrukuyik lakes so that total flux of biogeochemical solutes could be quantified. My exploration of how three subcatchments with varying amounts of stream-lake interactions revealed portions of the watershed that have less lake influence have more consistent biogeochemical conditions in the stream water than those with more stream-lake interactions. Yet, results from the spatial analysis included many findings that were subtle and not statistically robust, likely due to the limited amount of data available for the analysis. Hence, further synoptic data collection and analysis is necessary to produce greater confidence in interpreting the significance of stream-lake interactions in creating biogeochemical variability across the Oksrukuyik Creek watershed. I also explored how three lakes in Oksrukuyik Creek watershed that had very different size and volumes might have different effects on the biogeochemical signals leaving each lake. I found that clear evidence that increasing lake volume and residence time of water in a lake is related to an increased effect on the biogeochemical conditions leaving the lake. I also found evidence that there is a seasonal control on how strong an effect lakes have on biogeochemical outputs form lakes, with more biogeochemical changes occurring during the late thaw season. This spatial analysis of Oksrukuyik Creek indicates that biogeochemical signals moving through and therefore out of the watershed to downstream ecosystems are impacted by the abundance of stream-lake interactions and the size of lakes in the watershed.

The Arctic is undergoing drastic changes across space, but also through time. One such change that is occurring differentially across space but leads to rapid changes is the hydrologic "intensification" of the Arctic, where storm events are expected to increase in frequency and magnitude (Solomon et al., 2007; Rawlins et al., 2010; Bring et al., 2016; Bintanja et al., 2020). Storm events in the Arctic rapidly mobilize carbon and nutrients from the landscape to freshwater systems, resulting in large fluxes of biogeochemical concentrations that, for the most part, these rapid large fluxes have gone undocumented (Beel et al., 2020; Knapp et al., 2020). To further understand how Arctic stream-lake interactions are modulating the biogeochemical fluxes during storm events, I conducted a second stream-lake interaction study. In this second study I focused on stream-lake interaction biogeochemistry during storm events. The guiding research questions for this second study were: A) Does an Arctic lake change the riverine biogeochemical fluxes through a watershed during storm event flows?; and B) Do these storm events effects on biogeochemistry differ between early and late thaw season when thawed ground and terrestrial ecosystem conditions are vastly different? To address these questions, high-frequency biogeochemical sensors were installed at the inflow and outflow of a small Arctic Lake on the North Slope of Alaska (Lake I8) during the 2019 thaw season (June-September). These sensors collected DOC and NO_3^- concentrations (C) every 15 minutes and discharge (Q) every 10 minutes. Consequently, I was able to calculate relationships between C and Q during storms (i.e., a series of biogeochemical metrics). These results showed that the ecologically significant DOC and NO_3^- mobilization and transportation processes changed between the inflow and outflow of Lake I8. In general, the lake decreased the overall concentration variability moving into the lake, and it has the specific effect of reducing DOC and increasing NO_3^-. Interestingly, despite large changes in the terrestrial ecosystem during the thaw season, such as increasing thawed ground, changing light abundance, and shifts in plant conditions, the lake influence on DOC and NO_3^- did not change throughout the thaw season. Together, these specific stream-lake interaction effects observed in Lake I8 provide some of the first insights into how biogeochemical signals are modulated during thaw season storm events in the Arctic.

While these studies are based upon new and limited data sets of stream-lake interactions in the Arctic, the results provided insightful evidence for future studies in Arctic stream-lake interactions. The present work was limited by general assumptions, including residence time as a proxy for solute modulation, and lack of multi-year reproducibility. Hence, the results should not yet be over-interpreted or broadly applied to other Arctic watersheds. For example, the assumption of lake residence time and mixing used in my studies is an over-simplification, as mixing and stratification of lake waters not documented in our studies can impacted biogeochemical processes. Assessing historical records from one of our lakes (Lake I8) conducted prior to my studies, shows that Lake I8 is not universally mixing throughout the year with clear stratification occurring for much of the early thaw season. In addition, the morphology of Lake I8 illustrates that the inflow and outflow locations and the variable depth of the lake may not lead to complete mixing across the lake volume. Now that there is clear evidence that stream-lake interactions control watershed biogeochemistry, assessing how complex mixing, stratification, and lake morphology play a role in these biogeochemical controls are important factors for future assessment.

The thesis also focused on DOC and NO_3^-, so there are many other biogeochemical dimensions to explore in stream-lake interaction effects. Nevertheless, these two solutes of this thesis are master variables controlling aquatic ecosystems and provide valuable perspectives into nutrient changes within Arctic freshwater systems. Arctic DOC also plays an important role in global climate conditions as the export of DOC into watersheds and aquatic systems is known to impact the global carbon cycle (Battin et al., 2009; Goodman et al., 2011). In particular, permafrost in the Arctic is known to be a massive carbon storage reservoir (Tarnocai et al., 2009; Schuur et al., 2015; Turetsky et al., 2019), and this massive carbon reservoir is expected to change in extent and condition as climate change progresses (Jorgenson et al., 2010; Hobbie and Kling, 2014). The benefit of collecting high-frequency DOC in the Arctic is the ability to measure the release of carbon from the permafrost reservoir, track how carbon is mobilized, transported, and transformed throughout Arctic freshwater systems, and better understand how carbon moves between permafrost and the atmosphere. From this thesis, I found evidence that lakes modulate this DOC transport, which, on a larger scale, may impact total carbon export from Arctic landscapes. On the other hand, NO_3^- is a major limiting nutrient throughout Arctic freshwater systems. This limiting nutrient controls stream and lake metabolism, plus controls carbon and nutrient uptake. Measuring how NO_3^- changes over time provides insight into how freshwater productivity will change in Arctic stream-lake interactions.

The transport and transformation of carbon and nutrients from permafrost soils and through river networks remains uncertain (Kicklighter et al., 2013; Metcalf et al., 2018). Therefore, climate projections and models are actively developing and evolving. Data and results used in this study help inform how the lateral movement of biogeochemical solutes occurs in watersheds and, specifically, stream-lake interactions influence DOC and NO_3^- movement in and out of watersheds. Hence, as models advance and become more capable of representing more biogeochemical processes and smaller spatial scales, it may become possible to include stream networks and stream-lake interactions in assessing how a rapidly warming and hydrologically intensifying Arctic will alter both Arctic and global biogeochemical cycles that have huge impacts beyond the Arctic.

In summary, stream-lake interactions are a relatively small and complex part of Arctic and global scale ecological and climate conditions. However, climate change effects are ongoing and accelerating in the Arctic. Beyond the Arctic, climate change effects are readily seen in almost everyone’s lives, including dealing with heat waves, flooding, and drought. These changes are more pronounced in the Arctic though removed from the site of much of the global population. In the Arctic, warming is more than twice that of the global average, and storm events are increasing in frequency and intensity. These Arctic changes will have major consequences for Arctic permafrost, frozen ground which acts as a huge carbon and nutrient storage. This frozen ground currently locks away twice as much carbon as what is currently in the atmosphere. Permafrost is undergoing a thawing process, where carbon and nutrients are released, transported through aquatic ecosystems, and potentially released into the atmosphere or oceans, which may intensify climate change related disasters across the planet. Streams and lakes play a big role in the fate of the permafrost carbon and nutrients stored in the ground, as they are the drainage network that connect land to sea. Hence, research that builds our understanding of how streams and lakes control the movement of water, carbon, and nutrients through the globally important Arctic region is relevant to global climate change and people around globe.

Studies located in temperate regions have shown that stream networks, especially those that have lakes within the river network (i.e., stream-lake interactions) can change the amount and timing of carbon and nitrogen movement from land to sea.. Here I sought to reveal how stream-lake interactions in Arctic watersheds specifically change the amount and timing of carbon and nitrogen moving through Arctic watersheds. The results of this study found evidence that stream-lake interactions in Arctic watersheds does in fact control the amount and timing of carbon and nitrogen movement through river networks. This thesis is just one of many early steps on the path to understanding how stream-lake interactions change carbon and nitrogen export from Arctic landscapes, and advancing our ability to model and predict how a warming and hydrologically intensifying Arctic is for the fate of Arctic ecosystems and global climate change.

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